

Dearomatisation of 2-Naphthol by Oxidative Nucleophilic Substitution: an Efficient Two-step Process

Derek H. R. Barton,* Reine-Marie Bergé-Lurion, Xavier Lusinchi, and B. Mario Pinto*
Institut de Chimie des Substances Naturelles, C.N.R.S., 91190 Gif-sur-Yvette, France

An efficient synthesis of 1,1-dimethoxynaphthalen-2(1*H*)-one (**13**) has been achieved. Oxidation of 2-naphthol with bis-*p*-nitrobenzoyl peroxide gave the known derivative (**5**). Methylation with diazomethane and hydrolysis afforded 1-methoxy-2-naphthol which was oxidised in methanol to the enone (**13**) in high yield. The synthesis could also be carried out with benzoyl peroxide, but with lower yields.

We have described¹ the direct conversion of 2-naphthol into naphthoquinone monoacetals by oxidative nucleophilic substitution reactions. While these reactions were of interest from a mechanistic view-point, they were often complicated by the formation of side products and were of limited preparative use. Evidence was presented¹ which suggested that the complications arose because (1) the radical formed in the initial stages of the reaction was not oxidised to the carbocation rapidly enough and underwent dimerisation or coupling reactions, (2) the intermediate carbocation was trapped by the naphthol itself, and (3) the subsequent reactions of the monoacetals themselves were as rapid as the initial oxidation of the β -naphthol. In view of the reported² conversion of certain hydroquinone monoethers into the corresponding quinone monoacetals, in the presence of a suitable oxidant and an alcohol, in high yield, it seemed reasonable to assume that the stabilisation of the intermediate carbocation by an ether function in these systems gave rise to rapid oxidative nucleophilic substitution reactions, thereby circumventing the above-mentioned problems. We chose, therefore, to investigate the oxidation of 1-methoxy-2-naphthol (**1**) to the naphthoquinone monoacetal and report herein the dearomatisation of 2-naphthol (**2**) by means of an efficient two-step process.

Several preparations of 1-methoxy-2-naphthol (**1**) have been reported in the literature.³⁻⁵ However, many of these procedures³ have resulted in low yields. Notable exceptions are (1) the conversion of 1-naphthol into the desired compound by Friedel-Crafts acylation, followed by methylation, Baeyer-Villiger oxidation, and hydrolysis of the resulting acetate⁴ and (2) the oxidation of β -naphthol with bis-*p*-nitrobenzoyl peroxide followed by methylation and deacylation.⁵ We have now reinvestigated the latter reaction.

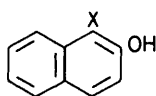
Treatment of 2-naphthol with bis-*p*-nitrobenzoyl peroxide⁶ in refluxing methylene chloride yielded a mixture of four components from which the major component could be fractionally crystallised. This was shown to be 2-*p*-nitrobenzoyloxy-1-naphthol (**5**) and presumably is derived from the initially formed 1-*p*-nitrobenzoyloxy-2-naphthol (**3**) by acyl migration. High performance liquid chromatography (h.p.l.c.) of the mother liquors afforded (**5**) (total yield 65%) as well as the remaining components; the latter were identified as being unchanged 2-naphthol (**2**) (23%), 1,1-bis-*p*-nitrobenzoyloxy-naphthalen-2(1*H*)-one (**9**) (1.6%), and 2,2-bis-*p*-nitrobenzoyloxynaphthalen-1(2*H*)-one (**11**) (8%). Compounds (**9**) and (**11**) were readily differentiated on the basis of their ¹H n.m.r. spectra. Thus, for example, the chemical-shift difference between 3-H and 4-H in the spectrum of (**9**) was 1.02 p.p.m., whereas the corresponding difference in that of (**11**) was 0.69 p.p.m. These values are typical of vinylic systems of enones and isolated double bonds, respectively. The formation of (**9**) and (**11**) from (**3**) and (**5**), respectively is analogous to the formation of products of this type in the lead tetra-acetate oxidation of naphthols.⁷

We have also investigated the corresponding reaction of 2-naphthol with benzoyl peroxide. In this case, however, attempts at fractional crystallisation were unsuccessful and h.p.l.c. was used to yield four components. These were identified as being 2-benzoyloxy-1-naphthol (**6**) [derived from (**4**) by acyl migration] (43%), unchanged 2-naphthol (23%), 1,1-dibenzoyloxy-naphthalen-2(1*H*)-one (**10**) (3.7%), and 2,2-dibenzoyloxy-naphthalen-1(2*H*)-one (**12**) (11.5%). It is noteworthy that the reaction of 2-naphthol with benzoyl peroxide has been described previously in the literature.⁸ The authors isolated a neutral compound to which they assigned the structure (**10**) (9.5% yield). In fact, the isomer obtained was the 2,2-dibenzoate (**12**).

Methylation of (**5**) and (**6**) with diazomethane yielded the 1-methoxy-2-acyloxy derivatives (**7**) and (**8**), respectively, both of which were subsequently hydrolysed to give 1-methoxy-2-naphthol (**1**).

We next turned our attention to the oxidative nucleophilic substitution reactions of 1-methoxy-2-naphthol (**1**). Thus, treatment of (**1**) with 1.1 equiv. of 2,3-dichloro-5,6-dicyano-benzoquinone (DDQ) in anhydrous methanol, for 5 min resulted in a near quantitative conversion into the dimethoxy acetal (**13**).¹ This contrasts with our previous work in which treatment of 2-naphthol with 2 equiv. of DDQ in anhydrous methanol afforded (**13**) in only 11% yield,¹ and supports the hypothesis that the stabilisation of the intermediate carbocation (**14**) by an ether function plays a significant role in the oxidative nucleophilic substitution reaction. The mechanisms of this reaction have been discussed previously.¹

We were also prompted to study the reaction of 1-methoxy-2-naphthol (**1**) in the presence of methanol with bis-*p*-

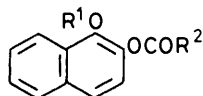


(1) X = OMe

(2) X = H

(3) X = *p*-NO₂C₆H₄CO₂

(4) X = PhCO₂

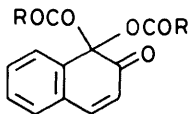


(5) R¹ = H, R² = *p*-NO₂C₆H₄

(6) R¹ = H, R² = Ph

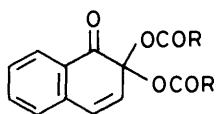
(7) R¹ = Me, R² = *p*-NO₂C₆H₄

(8) R¹ = Me, R² = Ph



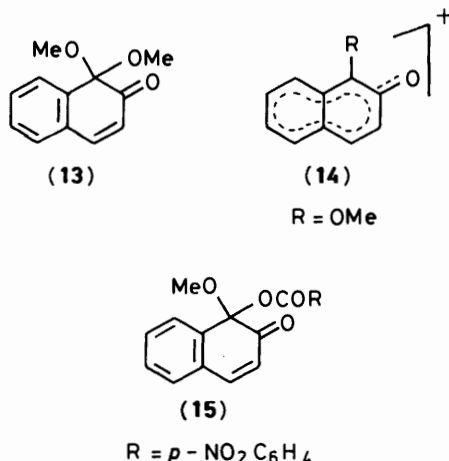
(9) R = *p*-NO₂C₆H₄

(10) R = Ph

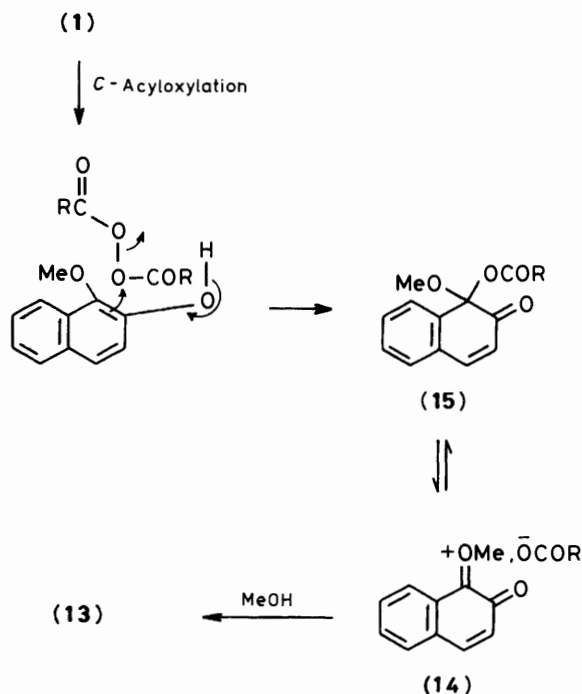


(11) R = *p*-NO₂C₆H₄

(12) R = Ph



nitrobenzoyl peroxide as oxidant. In this case the reaction did not proceed as cleanly as in the DDQ oxidation and chromatography was required to obtain the pure dimethoxy acetal (13); nonetheless, a yield of 85% was obtained. In a separate experiment this reaction was monitored carefully by t.l.c. and by ¹H n.m.r. spectroscopy. As the reaction progressed t.l.c. indicated the appearance of the dimethoxy acetal (13) and another component which disappeared gradually, giving rise to (13). Similarly, the ¹H n.m.r. spectrum indicated the presence of two AB systems attributable to vinyl protons of two different enones in the initial stages of the reaction but as time progressed, a decrease in intensity of the signals of one of these systems was observed together with a concomitant increase in intensity of the signals attributable to the vinyl protons of (13). We suggest, therefore, that the reaction proceeds *via* the intermediate, 1-methoxy-1-*p*-nitrobenzoyloxynaphthalen-2(1*H*)-one (15). An intermediate of this type has also been suggested in the lead tetra-acetate oxidation of 1-methoxy-2-naphthol.⁴ The reaction can be regarded as proceeding in a concerted fashion⁹ as shown in the Scheme or alternatively, by way of radical ion pairs.¹⁰



Scheme.

As a final point of interest, we examined the autoxidation of 1-methoxy-2-naphthol (1), catalysed by complexes of copper(II) chloride and pyridine. This type of reaction has been described¹¹ for phenols. Thus, treatment of (1) in anhydrous methanol and anhydrous pyridine containing copper(II) chloride in the presence of oxygen afforded 1,1-dimethoxy-naphthalen-2(1*H*)-one (13) in 80% yield after chromatography.

As expected on the basis of our previous work,¹ treatment of 2-naphthol itself under the conditions of the autoxidation reaction or with bis-*p*-nitrobenzoyl peroxide in the presence of methanol led to complex mixture of products, the dimethoxy acetal (13) being present only in small quantities.

Experimental

Melting points were determined in capillary tubes with a Büchi melting-point apparatus and are uncorrected. The i.r. spectra were recorded on a Perkin-Elmer 297 spectrophotometer. U.v. spectra were recorded on a Jobin Yvon Duospac 203 spectrophotometer. Mass spectra were recorded on a AEI MS 50 mass spectrometer under electron-impact conditions at 70 eV ionizing voltage. ¹H N.m.r. spectra were recorded on a Bruker WP 80 spectrometer. Chemical shifts are given in p.p.m. downfield from internal tetramethylsilane.

Analytical t.l.c. was performed on pre-coated glass plates with Merck silica gel 60F-254 as the adsorbent. The developed plates were air-dried, and exposed to u.v. light and/or sprayed with 60% aqueous sulphuric acid, and heated at 150 °C. Preparative t.l.c. was performed on 20 × 20 cm glass plates coated with silica gel (Kieselgel 60PF 254) as adsorbent (layer thickness 1.5 mm). H.p.l.c. was performed on a Waters Associated Prep LC/System 500 instrument with two Prep PAK-500 silica gel normal-phase columns and a refractive index detector. The chromatographic solvent system (A) was methylene chloride.

Solvents were distilled before use and were dried, as necessary, by literature procedures. Solvents were evaporated under reduced pressure and below 40 °C. Ether refers to diethyl ether and light petroleum to the fraction b.p. 40–60 °C.

Reactions performed under nitrogen were also carried out in deoxygenated solvents.

Reaction of 2-Naphthol with Bis-*p*-nitrobenzoyl Peroxide.—A mixture of bis-*p*-nitrobenzoyl peroxide (3.32 g, 0.01 mmol) and 2-naphthol (1.44 g, 0.01 mol) in dry methylene chloride (50 ml) was heated at reflux for 6 h under nitrogen. The yellow mixture was cooled, diluted with methylene chloride, and washed with aqueous sodium hydrogen carbonate and water. The organic layer was dried (Na₂SO₄) and the solvent evaporated to yield a yellow solid. T.l.c. (solvent A) indicated the presence of four components (*R_f* values 0.47, 0.33, 0.21, and 0.15). The solid was recrystallised from benzene to give yellow needles (1.7 g) which were shown by t.l.c. to consist of exclusively the most polar component (*R_f* 0.15). The filtrate was fractionated by h.p.l.c. using solvent A as eluant. The component having a *R_f* value of 0.15 was identified as 2-*p*-nitrobenzoyloxy-1-naphthol (5) (2.0 g, 65%), m.p. 182–183 °C (lit.,⁵ 182 °C); *v*_{max}. (CH₂Cl₂) 1745 (OCO) and 3570 cm⁻¹ (OH); δ_H (80 MHz; CDCl₃) 7.10–8.00 (5 H, m's, 5 × ArH), 8.12–8.62 (1 H, m, ArH), and 8.41 (4 H, 's', C₆H₄NO₂-*p*); *m/z* 309 (*M*⁺, 42%) and 150 (100). Compound (5) was converted into known 1-methoxy-2-naphthol (1) (see below).

The component having a *R_f* value of 0.21 was isolated as a white solid and was identified as being unchanged 2-naphthol (2) (0.33 g, 23%). The component having a *R_f* value of 0.33 was isolated as an off-white solid (discoloured with time) and was identified as being 1,1-bis-*p*-nitrobenzoyloxynaphthalen-2(1*H*)-one (9) (0.075 g, 1.6%). The sample was recrystallised

from acetone with difficulty to give white crystals, m.p. 260—261 °C (decomp.); ν_{\max} . (CH_2Cl_2) 1 740 (OCO) and 1 690 cm^{-1} (CO); λ_{\max} . (MeCN) 241 (ϵ 36 061), 260 (38 184), and 319 nm (11 397); δ_{H} (80 MHz; CDCl_3) 6.57 (1 H, d, J 10 Hz, 3-H), 7.59 (1 H, d, J 10 Hz, 4-H), 7.32—7.87 (3 H, m's, 3 \times ArH), 8.31 (8 H, 's', 2 \times p - $\text{O}_2\text{NC}_6\text{H}_4$), and 8.12—8.45 (1 H, m, 8-H); m/z 474 (M^+ , 22%), 300 (13), 130 (100), 120 (17), and 104 (86) (Found: M , 474.0675 (21.57%); base peak 130.0420 ($\text{C}_9\text{H}_6\text{O}^+$) (Calc. for $\text{C}_{24}\text{H}_{14}\text{N}_2\text{O}_9$: M , 474.0699).

The component having a R_f value of 0.47 was obtained as a pale yellow solid (discoloured with time) and was identified as being 2,2-bis- p -nitrobenzoyloxynaphthalen-1(2*H*)-one (11) (0.35 g, 8%). Recrystallisation from methylene chloride–pentane afforded off-white needles, m.p. 195—196 °C (decomp.); ν_{\max} . (CH_2Cl_2) 1 735 (OCO) and 1 705 cm^{-1} (CO); λ_{\max} . (MeCN) 239 (ϵ 42 199), 258 (35 461), and 332sh nm (4 078); δ_{H} (80 MHz; CDCl_3) 6.39 (1 H, d, J 10 Hz, 3-H), 7.08 (1 H, d, J 10 Hz, 4-H), 7.30—7.82 (3 H, m's, 3 \times ArH), 8.07—8.45 (1 H, m, 8-H), 8.29 (8 H, 's', 2 \times p - $\text{O}_2\text{NC}_6\text{H}_4$); m/z 474 (M^+ , 7%), 309 (14), 167 (100), 150 (100), and 130 (53) (Found: M , 474.0680. Calc. for $\text{C}_{24}\text{H}_{14}\text{N}_2\text{O}_9$: 474.0699).

Reaction of 2-Naphthol with Benzoyl Peroxide.—A mixture of benzoyl peroxide (2.42 g, 0.01 mol) and 2-naphthol (1.44 g, 0.01 mol) in dry methylene chloride (50 ml) was heated at reflux for 12 h. The deep red mixture was cooled and washed with aqueous sodium hydrogen carbonate and water. The organic layer was dried (Na_2SO_4) and the solvent evaporated to give a reddish foam (2.5 g) which was fractionated by h.p.l.c. using solvent A as eluant. Four components having R_f values 0.17, 0.20, 0.25, and 0.53 (solvent A) were isolated. The component having a R_f value of 0.17 was isolated as a solid and was identified as 2-benzoyloxy-1-naphthol (6) (1.14 g, 43%); ν_{\max} . (CH_2Cl_2) 1 735 (OCO) and 3 525 cm^{-1} (OH); δ_{H} (80 MHz; CDCl_3) 6.12 (1 H, br, OH), 7.12—7.90 (8 H, m's, 8 \times ArH), and 8.12—8.45 (3 H, m's, 3 \times ArH); m/z 264 (M^+ , 100%), 159 (11), and 131 (24). Compound (6) was converted into the known 1-methoxy-2-naphthol (1) (see below). The component having a R_f value of 0.20 was identified as being unchanged 2-naphthol (0.33 g, 23%). The component having a R_f value of 0.25 was obtained as a white solid and was identified as being 1,1-dibenzoyloxynaphthalen-2(1*H*)-one (10) (0.14 g, 3.7%). Recrystallisation from acetone afforded white prisms, m.p. 230 °C (decomp.); ν_{\max} . (CH_2Cl_2) 1 730 (OCO) and 1 690 cm^{-1} (CO); λ_{\max} . (MeCN) 238 (ϵ 40 611) and 324 (7 941); δ_{H} (80 MHz; CDCl_3) 6.59 (1 H, d, J 10 Hz, 3-H), 7.13—7.8 (9 H, m's, 4-H, 9 \times ArH), and 7.8—8.2 (5 H, m's, 5 \times ArH); m/z 384 (M^+ , 3%), 130 ($\text{C}_9\text{H}_6\text{O}^+$, 26), and 105 (100) [Found: M , 384.1009 (2.72%); base peak 105.0345 ($\text{C}_7\text{H}_5\text{O}^+$). Calc. for $\text{C}_{24}\text{H}_{16}\text{O}_5$: M , 384.0997]. The least polar component (R_f 0.53) was obtained as a white solid that discoloured with time. It was identified as being 2,2-dibenzoyloxynaphthalen-1(2*H*)-one (12) (0.44 g, 11.5%). Recrystallisation from acetone yielded white prisms, m.p. 187—188 °C; ν_{\max} . (CH_2Cl_2) 1 725 (OCO) and 1 700 cm^{-1} (CO); λ_{\max} . (MeCN) 241 (ϵ 68 852), 277 (6 580), 283sh (6 287), and 333 nm (2 704); δ_{H} (80 MHz; CDCl_3) 6.29 (1 H, d, J 10 Hz, 3-H), 6.96 (1 H, d, J 10 Hz, 4-H), 7.17—7.75 (9 H, m's, 9 \times ArH), and 7.92—8.30 (5 H, m's, 5 \times ArH); m/z 384 (M^+ , 1%), 130 (5), and 105 (100) [Found: M , 384.0993 (1.29%); base peak 105.0338 ($\text{C}_7\text{H}_5\text{O}^+$). Calc. for $\text{C}_{24}\text{H}_{16}\text{O}_5$: M , 384.0997].

1-Methoxy-2-naphthol (1).—(a) To a solution of 2- p -nitrobenzoyloxy-1-naphthol (5) (3.65 g, 11.8 mmol) in ether (500 ml) was added a 0.3*M*-solution of diazomethane in ether in portions with stirring while the reaction was monitored by t.l.c. (solvent A). The gradual disappearance of the starting material (R_f 0.15) and the appearance of a less polar component (R_f 0.67) was

observed. Upon completion of the reaction, the mixture was cooled and the excess of diazomethane was destroyed by addition of 10% hydrochloric acid. The layers were separated and the organic layer was washed successively with 10% aqueous sodium hydroxide and saturated aqueous sodium chloride. The ether layer was dried (Na_2SO_4) and the solvent was evaporated to afford a yellow solid (3.43 g, 90%). Recrystallisation from ethanol afforded 1-methoxy-2- p -nitrobenzoyloxynaphthalene (7) as bright yellow needles, m.p. 138—139 °C; ν_{\max} . (CH_2Cl_2) 1 740 cm^{-1} (OCO); δ_{H} (80 MHz; CDCl_3) 3.95 (3 H, s, OCH_3), 7.20—8.57 (6 H, m's, 6 \times ArH), and 8.35 (4 H, 's', p - $\text{O}_2\text{NC}_6\text{H}_4$); m/z 323 (M^+ , 100%), 173 (M^+ p - $\text{O}_2\text{NC}_6\text{H}_4\text{CO}$, 77), and 150 (83). Compound (7) (1.0 g, 3.10 mmol) was treated with potassium hydroxide (5 g) in methanol–water (9:1 v/v) (100 ml) at 60 °C for 2 h. The methanol was evaporated and the residue was acidified by addition of 2-*M*-hydrochloric acid. Methylene chloride was then added and the organic layer was washed with aqueous sodium hydrogen carbonate and water. The organic layer was dried (Na_2SO_4) and concentrated to afford a light beige solid (0.515 g) that was homogeneous by t.l.c. (R_f 0.46, solvent A). Recrystallisation from light petroleum yielded 1-methoxy-2-naphthol (1) as white needles, m.p. 91—92 °C (lit.,⁷ 92.5—93 °C); ν_{\max} . (CH_2Cl_2) 3 520 cm^{-1} (OH); δ_{H} (80 MHz; CDCl_3) 3.97 (3 H, s, OCH_3), 5.77 (1 H, s, OH), and 7.12—8.07 (6 H, m's, 6 \times ArH); m/z 174 (M^+ , 90%), 159 (100), and 131 (60).

(b) To a solution of 2-benzoyloxy-1-naphthol (6) (0.2 g, 0.76 mmol) in ether (30 ml) was added a 0.3*M*-solution of diazomethane in ether in portions with stirring while the reaction was monitored by t.l.c. (solvent A). The gradual disappearance of the starting material and the appearance of a less polar component (R_f 0.54) was observed. Upon completion of the reaction, the mixture was cooled and the excess of diazomethane was destroyed by addition of 10% hydrochloric acid. The layers were separated and the organic layer was washed successively with 10% aqueous sodium hydroxide and saturated aqueous sodium chloride. The ether layer was dried (Na_2SO_4) and the solvent was evaporated to afford a white solid that was identified as 2-benzoyloxy-1-methoxynaphthalene (8) (0.19 g, 90%), m.p. 108 °C (light petroleum) (lit.,⁵ 107 °C); ν_{\max} . (CH_2Cl_2) 1 735 cm^{-1} (OCO); δ_{H} (80 MHz; CDCl_3) 4.00 (3 H, s, OCH_3), 7.30—8.0 (8 H, m's, 8 \times ArH), and 8.0—8.45 (3 H, m's, 3 \times ArH); m/z 278 (M^+ , 100%). Compound (8) (0.19 g, 0.68 mmol) was treated with potassium hydroxide (0.9 g) in methanol–water (9:1) (20 ml) at 60 °C for 3 h. The mixture was concentrated to a volume of 3 ml, water was added, and the mixture was then acidified by addition of 2*M*-hydrochloric acid. The mixture was dissolved in methylene chloride and the organic layer was washed successively with aqueous sodium hydrogen carbonate and water and dried (Na_2SO_4). Evaporation of the solvent afforded a solid (0.112 g). Recrystallisation from light petroleum yielded 1-methoxy-2-naphthol (1) as white needles, m.p. 91—92 °C.

Reaction of 1-Methoxy-2-naphthol (1) with 2,3-Dichloro-5,6-dicyanobenzoquinone in Methanol.—To a stirred solution of (1) (0.85 g, 4.90 mmol) in anhydrous methanol (190 ml) under nitrogen was added 2,3-dichloro-5,6-dicyanobenzoquinone (1.2 g, 5.0 mmol). The mixture turned violet immediately and then the colour changed to orange. After 5 min the mixture was diluted with methylene chloride and washed successively with 5% aqueous sodium hydroxide, aqueous sodium hydrogen carbonate, water, and saturated aqueous sodium chloride. The organic layer was dried (Na_2SO_4) and the solvent was evaporated to yield a yellow liquid. T.l.c. (solvent A) and the ^1H n.m.r. spectrum indicated that 1,1-dimethoxynaphthalen-2(1*H*)-one (13)¹ was present as the sole product (0.97 g, 97%).

Reaction of 1-Methoxy-2-naphthol (1) with Bis-p-nitrobenzoyl Peroxide and Methanol.—A mixture of (1) (0.05 g, 0.287 mmol) and bis-*p*-nitrobenzoyl peroxide (0.095 g, 0.287 mmol) in anhydrous methanol (5 ml) and anhydrous methylene chloride (2 ml) was heated at 50 °C under nitrogen for 12 h. The mixture was diluted with methylene chloride and washed successively with aqueous sodium hydrogen carbonate and water. The organic layer was dried (Na₂SO₄) and the solvent evaporated to give a syrup that was purified by preparative t.l.c. using solvent A as eluant. 1,1-Dimethoxynaphthalen-2(1*H*)-one (13) was obtained as a yellow liquid (0.05 g, 85%).

In a separate experiment, a mixture of 1-methoxy-2-naphthol (1) (0.025 g, 0.143 mmol) and bis-*p*-nitrobenzoyl peroxide (0.048 g, 0.143 mmol) in [²H₁]chloroform (1 ml) and [²H₄]methanol (1 ml) was heated at 50 °C and the progress of the reaction was monitored by t.l.c. and by ¹H n.m.r. spectroscopy. After 1 h, t.l.c. indicated the presence of the starting material, the dimethoxy acetal (13), and a less polar component (*R*_f 0.51, solvent A). The ¹H n.m.r. spectrum indicated the presence of two doublets at δ 6.06 (*J* 10 Hz) and δ 6.20 (*J* 10 Hz) attributable to vinyl protons of two different enones and three singlets at δ 3.22, 3.55, and 3.92. As the reaction progressed, t.l.c. indicated the complete disappearance of the starting materials, the gradual disappearance of the component having an *R*_f value of 0.51, and the predominance of the dimethoxy acetal (13). The ¹H n.m.r. spectrum showed a decrease in intensity of the vinyl signal at δ 6.20 and a concomitant increase in intensity of the vinyl signal at δ 6.06. After 9 h t.l.c. and the ¹H n.m.r. spectrum revealed the presence of the dimethoxy acetal (13) and *p*-nitrobenzoic acid only.

Copper–Amine Catalysed Autoxidation of 1-Methoxy-2-naphthol (1).—To a solution of (1) (0.1 g, 0.57 mmol) in anhydrous methanol (6 ml) and anhydrous pyridine (2 ml) was added copper(II) chloride (0.020 g) and the mixture was stirred at ambient temperature. After a few minutes an intense pink–purple colour appeared. As time progressed the colour changed to yellow and then to blue–green. After 12 h, t.l.c. (solvent A)

indicated the presence of the starting material and a more polar component. Copper(II) chloride (0.010 g) was added and air was bubbled through the mixture intermittently. After an additional 12 h, t.l.c. indicated the absence of starting material. The mixture was poured into water and the aqueous layer was thoroughly extracted with methylene chloride. The extracts were washed with saturated aqueous sodium chloride and dried over anhydrous sodium sulphate. The solvent was evaporated to yield a liquid which was purified by preparative t.l.c. using solvent A as eluant. 1,1-Dimethoxynaphthalen-2(1*H*)-one (13) was obtained as a yellow liquid (0.093 g, 80%).

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