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The Oxidation of Some Naphthols with Benzoyl Peroxide

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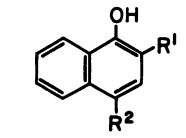
The reactions of four naphthols (1-naphthol (**1**), 2-naphthol (**2**), 4-isopropyl-1-naphthol (**18**), and 3-isopropyl-2-naphthol (**19**)) with benzoyl peroxide were examined under two reaction conditions (A and B). Each of the naphthols **1**, **2**, **18**, and **19** was oxidized with 0.95 equivalent moles of benzoyl peroxide at room temperature for 24 h (condition A) to give mainly the corresponding ortho-benzoyloxylated product which was isolated in moderate yield as an equilibrium mixture, resulting from its trans-benzoylation. The naphthols **18** and **19** were also oxidized with 2.25 equivalent moles of benzoyl peroxide at room temperature for 48 h (condition B) to give mainly 2,2-bis(benzoyloxy)-4-isopropyl-1(2*H*)-naphthalenone and 2,2-bis(benzoyloxy)-3-isopropyl-1(2*H*)-naphthalenone in good yields. The oxidations of **1** and **2** under condition B produced the same product, 2,2-bis(benzoyloxy)-1(2*H*)-naphthalenone, in low yields.

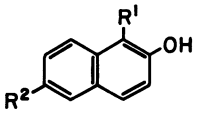
Although the oxidation of various phenols with benzoyl peroxide has been considerably investigated,[1,2] comparatively little research has been performed on the oxidation of naphthol compounds. In 1963, Edward and Samad[3] reported that both 1-naphthol (**1**) and 2-naphthol (**2**) yielded the same product, 2-(4-nitrobenzoyloxy)-1-naphthol (**3**), through oxidation with bis(4-nitrobenzoyl) peroxide in refluxing chloroform. However, when benzoyl peroxide was used, the corresponding benzoyloxy derivative could not be obtained. Bhatia and Mathur[1,4] also reported the oxidation of **2** with benzoyl peroxide in refluxing chloroform; they obtained a trace of 1-benzoyloxy-2-naphthol (**4**) and a small amount (1% yield) of 1,1-bis(benzoyloxy)-2(1*H*)-naphthalenone (**5**), the revised structure of which is described later. A similar oxidation[5] of **1** produced 4,4′-dihydroxy-1,1′-binaphthyl (**6**: 45%) and 1,4-naphthoquinone (**7**: 16%). However, 1-bromo-2-naphthol (**8**)[5] yielded only 1,2-naphthoquinone (**9**) in 25% yield. Mathur et al. further demonstrated the oxidations of two more bromonaphthols in refluxing chloroform. That is, 4-bromo-1-naphthol (**10**)[6] produced three compounds: 2-benzoyloxy-4-bromo-1-naphthol (**11**: 6%), 1,2-bis(benzoyloxy)-4-bromonaphthalene (**12**: 2%), and 2-benzoyloxy-1,4-naphthoquinone (**13**). On the other hand, 6-bromo-2-naphthol (**14**)[7] afforded two compounds: 1-benzoyloxy-6-bromo-2-naphthol (**15**: 13%) and 1,1-bis(benzoyloxy)-6-bromo-2(1*H*)-naphthalenone (**16**: 4%).

In connection with our synthetic study[8] of the natural coleon A (**17**),[9-11] we have also investigated the oxidations of various naphthol compounds with benzoyl peroxide in order to obtain further information on the introduction of oxygen functions in the naphthol skeleton. This paper describes the reactions of 1-naphthol (**1**), 2-naphthol (**2**), 4-isopropyl-1-naphthol (**18**), and 3-isopropyl-2-naphthol (**19**) with benzoyl peroxide.

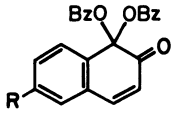
Each of the naphthols was oxidized under two reaction conditions (A and B); the results are



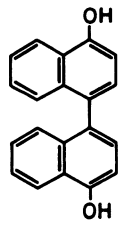
1 $R^1=R^2=H$
3 $R^1=OCOC_6H_4NO_2(p)$, $R^2=H$
10 $R^1=H$, $R^2=Br$
11 $R^1=OBz$, $R^2=Br$



2 $R^1=R^2=H$
4 $R^1=OBz$, $R^2=H$
8 $R^1=Br$, $R^2=H$
14 $R^1=H$, $R^2=Br$
15 $R^1=OBz$, $R^2=Br$



5 R=H
16 R=Br



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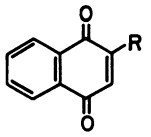
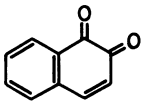


7 R=H
13 R=OBz



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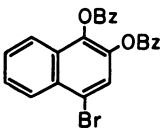

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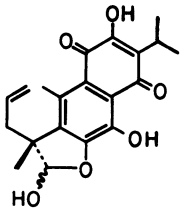

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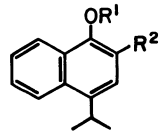
summarized in Table 1.

The oxidation of 1-naphthol (**1**) with 0.95 equivalent moles of benzoyl peroxide in dichloromethane at room temperature for 24 h (condition A) afforded a ca. 1:1 mixture (25%) of 1-benzoyloxy-2-naphthol (**4**) and 2-benzoyloxy-1-naphthol (**20**), together with 2,2-bis(benzoyloxy)-1(2*H*)-naphthalenone (**21**: 4%), 4-benzoyloxy-1-naphthol (**22**: 3%), and the starting **1** (16%). However, the oxidation of **1** with 2.25 equivalent moles of benzoyl peroxide in dichloromethane at room temperature for 48 h (condition B) afforded a complicated mixture, from which **21** and 2-benzoyloxy-1,4-naphthoquinone (**13**) were isolated in low yields of 6 and 5%, respectively.

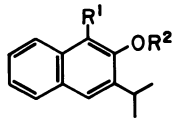
Similarly, 2-naphthol (**2**) was oxidized under condition A to give a ca. 1:1 mixture (52%) of **4** and **20**, **21** (8%), 1,1-bis(benzoyloxy)-2(1*H*)-naphthalenone (**5**: 3%), and the starting **2** (28%). Under condition B, **2** produced **21** and **5** in 26 and 6% yields, respectively.

The oxidation of 4-isopropyl-1-naphthol (**18**) under condition A afforded a ca. 2:3 mixture (42%) of 2-benzoyloxy-4-isopropyl-1-naphthol (**23**) and 1-benzoyloxy-4-isopropyl-2-naphthol (**24**), along with 2,2-bis(benzoyloxy)-4-isopropyl-1(2*H*)-naphthalenone (**25**: 14%), 4,4′-diisopropyl-2,2′-bi-1-naphthol (**26**: 7%), and a trace of 1,1′,2,2′-tetrahydro-4,4′-diisopropyl-1,1′-dioxo-2,2′-binaphthylidene (**27**: 1%). However, when **18** was oxidized under condition B, it gave a ca. 2:3 mixture (4%) of **23** and **24**, **25** (65%), **27** (3%), and 1,1-bis(benzoyloxy)-4-isopropyl-2(1*H*)-naphthalenone (**28**: 4%).

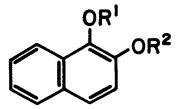
3-Isopropyl-2-naphthol (**19**) was also oxidized



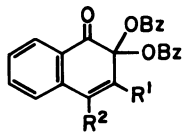
18 R¹=R²=H
23 R¹=H, R²=OBz
24 R¹=Bz, R²=OH
38 R¹=Bz, R²=OAc



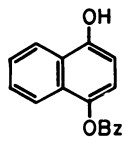
19 R¹=R²=H
29 R¹=OH, R²=Bz
30 R¹=OBz, R²=H
39 R¹=OAc, R²=Bz



20 R¹=H, R²=Bz
33 R¹=Ac, R²=Bz
34 R¹=Bz, R²=Ac



21 R¹=R²=H
25 R¹=H, R²=i-Pr
31 R¹=i-Pr, R²=H



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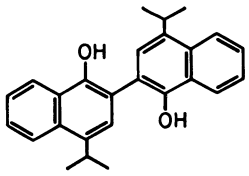

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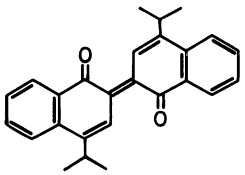

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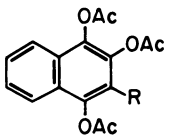
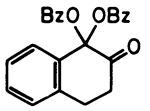
28 R¹=H, R²=i-Pr
32 R¹=i-Pr, R²=H



35 R=H
41 R=i-Pr



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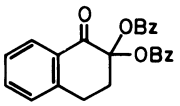

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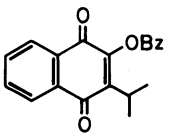

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Table 1. Oxidations of Naphthols with Benzoyl Peroxide in Dichloromethane at Room Temperature

Substrate	Condition[a]	Product (Yield/%)			
1	A	**4**+**20** (25)	**21** (4)	**22** (3)	—
	B	—	**21** (6)	—	**13** (5)
2	A	**4**+**20** (52)	**21** (8)	**5** (3)	—
	B	—	**21** (26)	**5** (6)	—
18	A	**23**+**24** (42)	**25** (14)	**26** (7)	**27** (1)
	B	**23**+**24** (4)	**25** (65)	**28** (4)	**27** (3)
19	A	**29**+**30** (66)	**31** (9)	—	—
	B	**29**+**30** (5)	**31** (65)	**32** (14)	—

a) A: 0.95 equivalent moles of benzoyl peroxide for 24 h. B: 2.25 equivalent moles of benzoyl peroxide for 48 h.

under condition A to give a ca. 1:1 mixture (66%) of 2-benzoyloxy-3-isopropyl-1-naphthol (**29**) and 1-benzoyloxy-3-isopropyl-2-naphthol (**30**), 2,2-bis(benzoyloxy)-3-isopropyl-1(2*H*)-naphthalenone (**31**: 9%), and the starting **19** (16%). The oxidation of **19** under condition B produced a ca. 1:1 mixture (5%) of **29** and **30**, **31** (65%), and 1,1-bis(benzoyloxy)-3-isopropyl-2(1*H*)-naphthalenone (**32**: 14%). The structures of the oxidation products were determined by the following chemical and spectroscopic studies.

Phenolic compounds, **4** and **20**, were obtained as a mixture (ca. 1:1), whose IR spectrum indicated the presence of hydroxyl (3575 and 3280 cm^{-1}) and benzoyloxyl (1745 cm^{-1}) groups. The ^1H NMR spectrum of the mixture showed doublet signals due to C-3 and C-4 protons at δ 7.22 and 7.65 for **4** and at δ 7.30 and 7.46 for **20**. The difference in these chemical shifts of the C-4 protons is obviously attributable to the C-1 substituent (hydroxyl or benzoyloxyl group): the presence of a hydroxyl group at the C-1 position causes an upfield shift of the C-4 proton. Therefore, the structures of **4** and **20** were assigned to be 1-benzoyloxy-2-naphthol and 2-benzoyloxy-1-naphthol, respectively. Acetylation of the mixture (ca. 1:1) with isopropenyl acetate and *p*-toluenesulfonic acid in refluxing toluene afforded two separable acetates,[12] **33** and **34**, in 28 and 71% yields. The ^1H NMR spectrum of **33** indicated signals due to an acetoxy methyl at δ 2.30 (singlet) and a C-3 aromatic proton at δ 7.43 (doublet, J=9 Hz), while that of **34** indicated the corresponding signals at δ 2.16 (singlet) and 7.35 (doublet, J=9 Hz). Since the acetoxy methyl and the C-3 proton in **33** were more deshielded than those in **34** by the effect of aromatic rings, the structures of **33** and **34** were assigned to be 1-acetoxy-2-benzoyloxynaphthalene and 2-acetoxy-1-benzoyloxynaphthalene, respectively.

Compound **21** (mp 195—196 °C) showed absorption bands at 1732 and 1709 cm^{-1} in its IR spectrum, indicating the presence of benzoyloxyl groups and a conjugated carbonyl group. The ^1H NMR spectrum of **21** showed two doublet signals due to C-3 and C-4 olefinic protons at δ 6.33 and 6.98.

Compound **5** (mp 239—240 °C) also showed similar spectral data: IR 1736 and 1695 cm^{-1}, ^1H NMR δ 6.56 and 7.50 (each 1 H and doublet). Comparisons of these spectral data with those of **21** suggested that the carbonyl group in **5** is conjugated with the C-3 and C-4 double bond. To obtain a further confirmation on the structures of **5** and **21**, the following reactions were carried out. Compounds **5** and **21** were each treated with acetic anhydride containing concentrated sulfuric acid to give the same product, 1,2,4-triacetoxynaphthalene (**35**),[4] in 90 and 73% yields, respectively. The catalytic hydrogenation of **5** over 5% Rh–Al_2O_3 in 1,4-dioxane afforded the corresponding tetrahydro ketone (**36**: 32%), along with a mixture of the phenolic compounds (**4** and **20**: 66%). This ketone **36** showed the presence of a nonconjugated carbonyl group (1727 cm^{-1}) in its IR spectrum. A similar catalytic hydrogenation of **21** also afforded the tetrahydro compound (**37**: 60%) and a mixture of **4** and **20** (38%). The IR spectrum of **37** showed absorption bands at 1735 and 1710 cm^{-1}, indicating the presence of benzoyloxyl groups and a conjugated carbonyl group. Thus, the structures of **5** and **21** were assigned to be 1,1-bis(benzoyloxy)-2(1*H*)-naphthalenone and 2,2-bis(benzoyloxy)-1(2*H*)-naphthalenone, respectively.

Bhatia and Mathur[4] prepared the bis(benzoyloxy)-naphthalenone derivative (mp 186—187 °C) and proposed its structure as being **5**. However, the reported melting point is quite different from that of **5**, but similar to that of **21**. For a direct comparison with the product of Bhatia and Mathur, 2-naphthol (**2**) was also oxidized under their reaction condition using one equivalent mole of benzoyl peroxide in refluxing chloroform[4] to give 2,2-bis(benzoyloxy)-1(2*H*)-naphthalenone (**21**: mp 195—196 °C) in 7.5% yield. Therefore, the proposed structure **5** must be revised to **21**.

Compound **22** showed the presence of a hydroxyl group (3580 and 3320 cm^{-1}) and a benzoyloxyl group (1730 cm^{-1}) in its IR spectrum. The ^1H NMR spectrum of **22** showed signals due to a pair of ortho-coupling aromatic protons at δ 6.61 and 7.07 (each 1H, doublet, and J=8 Hz). Thus, the structure of **22** was assigned to be 4-benzoyloxy-1-naphthol.

Compound **13** showed the presence of a benzoyloxyl group (IR 1749 cm^{-1}) and a *p*-quinone moiety [IR 1667 cm^{-1}, ^1H NMR δ 6.93 (1H, singlet, C-3 proton)]. This compound was also obtained by the oxidation of a phenolic mixture (**4** and **20**) with Jones reagent in 14% yield or by the oxidation of the naphthalenone compound **21** with *m*-chloroperbenzoic acid in 22% yield. Thus, the structure of **13** was assigned to be 2-benzoyloxy-1,4-naphthoquinone.

Phenolic compounds, **23** and **24**, were obtained as a mixture (ca. 2:3), the IR spectrum of which indicated the presence of hydroxyl (3570 and 3320 cm^{-1}) and benzoyloxyl (1740 cm^{-1}) groups. The ^1H NMR spectrum of the mixture showed signals due to hydroxyl, C-3, and C-8 protons at δ 6.10 (broad), 7.19 (singlet), and 8.31 (multiplet) for the minor phenol **23**, and at δ 5.85 (broad), 7.19 (singlet), and 7.84 (multiplet) for the major phenol **24**. The appearance of the C-8 proton signal of **23** in a very low field (δ 8.31) suggested the presence of a hydroxyl group at the C-1 position. Thus, the structures of **23** and **24** were assigned to be 2-benzoyloxy-4-isopropyl-1-naphthol and 1-benzoyloxy-4-isopropyl 2-naphthol, respectively. Acetylation of the mixture (**23** and **24**) with isopropenyl acetate and *p*-toluenesulfonic acid in refluxing toluene afforded an acetate (64%), the

structure of which was assigned to be 2-acetoxy-1-benzoyloxy-4-isopropylnaphthalene (**38**) by comparisons of its ^{1}H NMR spectrum with those of **33** and **34**. The hydrolysis of **38** with dilute hydrochloric acid in refluxing methanol produced **24** containing a small amount of **23**. This was dissolved in deuteriochloroform and then allowed to stand at room temperature for 24 h to give an equilibrium mixture of **23** and **24** (ca. 2:3).[13]

Compound **25** indicated the presence of benzoyloxyl groups (1727 cm^{-1}) and a conjugated carbonyl group (1703 cm^{-1}) in its IR spectrum. The ^{1}H NMR spectrum of **25** showed a singlet signal due to a C-3 olefinic proton at δ 6.18. Thus, the structure of **25** was assigned to be 2,2-bis(benzoyloxy)-4-isopropyl-1(2*H*)-naphthalenone. This structure was further supported by its UV spectrum (Fig. 1).

Compound **26** was identified as 4,4′-diisopropyl-2,2′-bi-1-naphthol by the following spectral data; MS *m/z* 370 (M$^+$), IR 3535 and 3270 cm^{-1}, and ^{1}H NMR δ 5.56 (singlet, hydroxyls) and 7.32 (singlet, C-3 and C-3′ protons).

Compound **27**, IR 1629 cm^{-1} (conjugated carbonyls) and ^{1}H NMR δ 8.29 (singlet, C-3 and C-3′ protons), was also obtained by the oxidation of **26** with potassium hexacyanoferrate(III) in an alkaline solution in 81% yield. Thus, the structure of **27** was assigned to be 1,1′,2,2′-tetrahydro-4,4′-diisopropyl-1,1′-dioxo-2,2′-binaphthylidene.

Compound **28** showed the presence of benzoyloxyl groups (1737 cm^{-1}) and a conjugated carbonyl group (1680 cm^{-1}) in the IR spectrum. Its ^{1}H NMR spectrum showed a singlet signal due to a C-3 olefinic proton at δ 6.51. Thus, the structure of **28** was assigned to be 1,1-bis(benzoyloxy)-4-isopropyl-2(1*H*)-naphthalenone. This structure was further supported by its UV spectrum (Fig. 2).

Phenolic compounds, **29** and **30**, were obtained as a mixture (ca. 1:1), the IR spectrum of which indicated the presence of hydroxyl (3575 and 3320 cm^{-1}) and benzoyloxyl (1737 cm^{-1}) groups. Recrystallization of the mixture afforded pure crystalline **30**. The ^{1}H NMR spectrum of **30** showed a singlet signal due to a C-4 aromatic proton at δ 7.60, while that of **29** showed a corresponding signal at δ 7.38. The appearance of the C-4 proton signal of **29** in a high field suggested the presence of a hydroxyl group at the C-1 position. Thus, the structures of **29** and **30** were assigned to be 2-benzoyloxy-3-isopropyl-1-naphthol and 1-benzoyloxy-3-isopropyl-2-naphthol, respectively. Acetylation of the mixture (ca. 1:1) of **29** and **30** with isopropenyl acetate and *p*-toluenesulfonic acid in refluxing toluene afforded 1-acetoxy-2-benzoyloxy-3-isopropylnaphthalene (**39**: 76%),[12] which was hy-

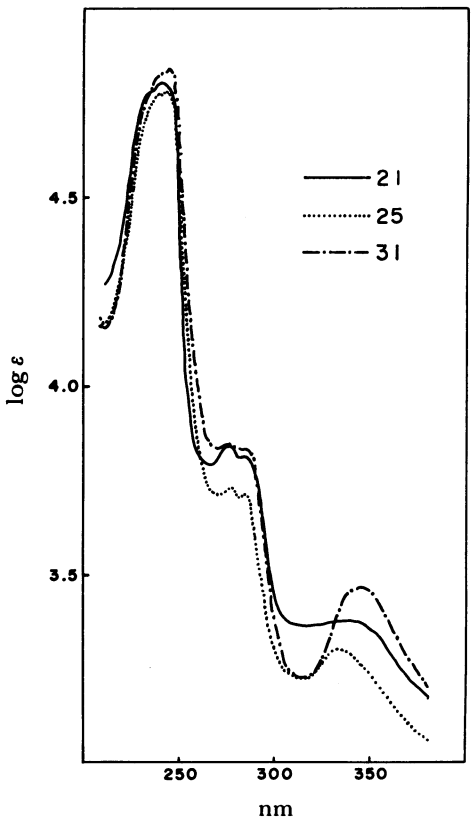

Fig. 1. The UV spectra of 2,2-bis(benzoyloxy)-1(2*H*)-naphthalenone derivatives **21**, **25**, and **31** in ethanol.

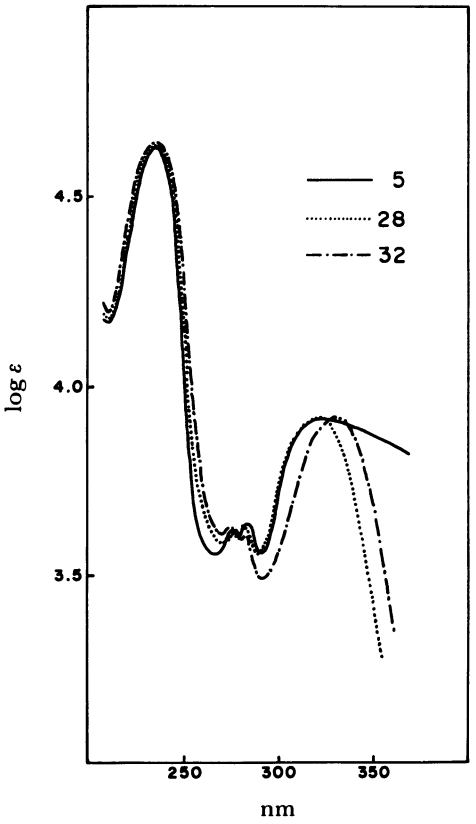

Fig. 2. The UV spectra of 1,1-bis(benzoyloxy)-2(1*H*)-naphthalenone derivatives **5**, **28**, and **32** in ethanol.

drolyzed with dilute hydrochloric acid in refluxing methanol to give **29** containing a small amount of **30**. This was dissolved in deuteriochloroform and then allowed to stand at room temperature for 24 h to give an equilibrium mixture of **29** and **30** (ca. 1:1).[13] Compound **30** was oxidized with Jones reagent to afford 2-benzoyloxy-3-isopropyl-1,4-naphthoquinone (**40**) in 32% yield.

Compound **31** indicated the presence of benzoyloxyl groups (1729 cm^{-1}) and a conjugated carbonyl group (1703 cm^{-1}) in the IR spectrum. Its ^1H NMR spectrum showed a singlet signal due to a C-4 olefinic proton at δ 6.88. Thus, the structure of **31** was assigned to be 2,2-bis(benzoyloxy)-3-isopropyl-1(2*H*)-naphthalenone. This structure was further supported by its UV spectrum (Fig. 1). The oxidation of **31** with *m*-chloroperbenzoic acid afforded the quinone **40** in 36% yield. Compound **31** was also treated with acetic anhydride containing concentrated sulfuric acid to give 1,2,4-triacetoxy-3-isopropylnaphthalene (**41**) in 86% yield.

Compound **32** was identified as 1,1-bis(benzoyloxy)-3-isopropyl-2(1*H*)-naphthalenone by the following spectral data: IR 1731 and 1683 cm^{-1}, ^1H NMR δ 7.23 (singlet, C-4 proton), and UV (Fig. 2). The treatment of **32** with acetic anhydride containing concentrated sulfuric acid produced the triacetate **41** in 83% yield.

As shown in Table 1, the naphthols **1**, **2**, **18**, and **19** were oxidized under condition A to give mainly the corresponding ortho-benzoyloxylated product which was isolated as an equilibrium mixture (**4**+**20**, **23**+**24**, and **29**+**30**), resulting from its trans-benzoylation. On the other hand, oxidations of these naphthols under condition B produced mainly the corresponding bis(benzoyloxy)naphthalenone derivatives **5**, **21**, **25**, **28**, **31**, and **32**, although in the case of **1** the yield was very low.

From the present study, it is clear that the benzoyl peroxide oxidation is effective for the introduction of oxygen functions to the naphthol skeleton, in contrast to the results of Edward and Samad,[3] and Mathur et al.[4-7]

Experimental

All melting points are uncorrected. The IR spectrum were measured in chloroform and the ^1H NMR spectra in deuteriochloroform at 90 MHz with tetramethylsilane as an internal standard unless otherwise stated; s: singlet, bs: broad singlet, d: doublet, dd: double doublet, m: multiplet. The column chromatography was performed using Merck silica gel (0.063—0.200 mm).

4-Isopropyl-1-naphthol (18). A solution of 4-acetyl-1-naphthol[14] (1.862 g) in dry tetrahydrofuran (20 ml) was added dropwise to a stirred ether solution of methylmagnesium iodide prepared from magnesium turnings (961 mg) and methyl iodide (2.49 ml) in dry ether (24 ml). The mixture was refluxed for 2 h, poured into a mixture of ice and aqueous ammonium chloride, and extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated in vacuo to give a crude 4-(1-hydroxy-1-methylethyl)-1-naphthol, IR 3600 and 3220 cm^{-1}.

The above crude product was refluxed with acetic anhydride (15 ml) and sodium acetate (3.0 g) for 7 h. After evaporation of the acetic anhydride in vacuo, the residue was diluted with water and extracted with ether. The ether extract was washed with aqueous sodium hydrogencarbonate and brine, dried, and evaporated in vacuo. The residue was chromatographed on silica gel (200 g), using benzene as an eluent, to give 1-acetoxy-4-isopropenylnaphthalene (2.163 g: 95.6%), IR 1765 cm^{-1}, ^1H NMR (60 MHz) δ=2.18 (3H, m, $C\underline{H}_3C(=CH_2)$), 2.44 (3H, s, $-OCOCH_3$), 5.03 (1H, m) and 5.37 (1H, m) ($-C(=CH_2)$), 7.17 and 7.29 (each 1H, d, and J=8.5 Hz, C_2-H and C_3-H), 7.30—7.65 (2H, m, C_6-H and C_7-H), 7.70—8.20 (2H, m, C_5-H and C_8-H).

A mixture of the above acetate (2.163 g), 5% Pd-C (540 mg), and concentrated hydrochloric acid (0.2 ml) in methanol (40 ml) was hydrogenated at room temperature under an atmosphere of hydrogen for 19 h. After the usual work-up, the crude product was chromatographed on silica gel (200 g), using benzene as an eluent, to give **18**[15] (1.430 g: 79.8%). This was recrystallized from hexane–cyclohexane, mp 65—66 °C, IR 3600 and 3325br cm^{-1}, ^1H NMR δ=1.35 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 3.64 (1H, m, $-C\underline{H}(CH_3)_2$), 5.17 (1H, bs, $-OH$), 6.74 (1H, d, J=8 Hz, C_2-H), 7.18 (1H, d, J=8 Hz, C_3-H), 7.33—7.52 (2H, m, C_6-H and C_7-H), and 7.96—8.28 (2H, m, C_5-H and C_8-H). Found: C, 83.75; H, 7.92%. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58%.

3-Isopropyl-2-naphthol (19). A solution of methyl 2-hydroxy-3-naphthoate (10.110 g) in dry ether (300 ml) was added dropwise to a stirred ether solution of methylmagnesium iodide prepared from magnesium turnings (7.292 g) and methyl iodide (18.7 ml) in dry ether (200 ml). The mixture was refluxed for 1.5 h, poured into a mixture of ice and aqueous ammonium chloride, and extracted with ether. The ether extract was washed with brine, dried, and evaporated in vacuo. The residue was refluxed with acetic anhydride (50 ml) and sodium acetate (15.0 g) for 7 h. After the work-up (as described above) the crude product was chromatographed on silica gel (250 g), using benzene as an eluent, to give 2-acetoxy-3-isopropenylnaphthalene (10.860 g: 96.0%), IR 1755 cm^{-1}, ^1H NMR (60 MHz) δ=2.12 (3H, bs, $C\underline{H}_3C(=CH_2)$), 2.28 (3H, s, $-OCOCH_3$), 5.11 (1H, m) and 5.21 (1H, m) ($-C(=CH_2)$), 7.30—7.58 (2H, m, C_6-H and C_7-H), 7.48 (1H, s, C_1-H), 7.58–7.90 (2H, m, C_5-H and C_8-H), and 7.72 (1H, s, C_4-H).

A mixture of the above acetate (10.860 g) and 5% Pd-C (2.80 g) in methanol (160 ml) was hydrogenated at room temperature under an atmosphere of hydrogen for 17 h to give 2-acetoxy-3-isopropylnaphthalene (10.366 g), IR 1750 cm^{-1}, ^1H MMR (60 MHz) δ=1.34 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 2.36 (3H, s, $-OCOCH_3$), 3.12 (1H, m, $-C\underline{H}(CH_3)_2$), 7.25—7.58 (2H, m, C_6-H and C_7-H), 7.48 (1H, s, C_1-H), 7.58—7.93 (2H, m, C_5-H and C_8-H), and 7.72 (1H, s, C_4-H).

The above crude acetate (10.366 g) was treated with lithium aluminium hydride (2.584 g) in dry ether (200 ml) at room temperature for 2 h. The mixture was poured into ice–aqueous ammonium chloride and extracted with ether. The ether extract was washed with brine, dried, and

evaporated in vacuo. The residue was chromatographed on silica gel (250 g), using benzene as an eluent, to give **19**[16] (7.562 g: 84.6%). This was recrystallized from hexane, mp 81—82 °C, IR 3590 and 3290 cm^{-1}, ^1H NMR δ=1.33 (6H, d, J=7 Hz, -CH(C<u>H</u>$_3$)$_2$), 3.33 (1H, m, -C<u>H</u>(CH$_3$)$_2$), 4.96 (1H, s, -OH), 6.98 (1H, s, C_1-H), 7.59 (1H, s, C_4-H), 7.14—7.45 (2H, m, C_6-H and C_7-H), and 7.45—7.80 (2H, m, C_5-H and C_8-H). Found: C, 83.97; H, 7.83%. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58%.

Oxidation of 1-Naphthol (1) with Benzoyl Peroxide. *a*): **The Condition A.** A solution of **1** (288.0 mg) and benzoyl peroxide (460.0 mg) in dichloromethane (6.0 ml) was protected from light and stirred at room temperature for 24 h. After the addition of ether (20 ml), acetic acid (0.2 ml), and aqueous potassium iodide (20%, 5.0 ml), the mixture was further stirred at room temperature for 3 h. The mixture was washed successively with water, aqueous sodium thiosulfate, and brine. The dried solution was evaporated in vacuo and the residue was chromatographed on silica gel (50 g), using hexane–benzene (1:1) as an eluent, to give the starting **1** (46.5 mg: 16.1%). Further elution with benzene and ether–benzene (1:99) afforded four compounds **4**, **20**, **21**, and **22**.

1-Benzoyloxy-2-naphthol (**4**) and 2-benzoyloxy-1-naphthol (**20**) in a ratio of ca. 1:1 (133.2 mg: 25.2%), mp 173—176 °C (ca. 1:1 mixture from chloroform), IR 3575, 3280br, and 1745 cm^{-1}. ^1H NMR of **4** δ=5.91 (1H, bs, C_2-OH), 7.22 (1H, d, J=8.5 Hz, C_3-H), 7.32—7.88 (7H, m, C_5-H, C_6-H, C_7-H, C_8-H, and C_3-H, C_4-H, C_5-H of benzoyloxyl group), 7.65 (1H, d, J=8.5 Hz, C_4-H), and 8.33 (2H, dd, J=8 and 2 Hz, C_2-H and C_6-H of benzoyloxyl group). ^1H NMR of **20** δ=6.18 (1H, bs, C_1-OH), 7.30 (1H, d, J=9 Hz, C_3-H). 7.32—7.88 (6H, m, C_5-H, C_6-H, C_7-H, and C_3-H, C_4-H, C_5-H of benzoyloxyl group), 7.46 (1H, d, J=9 Hz, C_4-H), 8.24 (2H, dd, J=8 and 2 Hz, C_2-H and C_6-H of benzoyloxyl group), and ca. 8.25 (1H, m, C_8-H). Found: C, 77.41; H, 4.43%. Calcd for $C_{17}H_{12}O_3$: C, 77.26; H, 4.58%.

2,2-Bis(benzoyloxy)-1(2*H*)-naphthalenone (**21**) (27.9 mg: 3.6%), mp 195—196 °C decomp (from acetone), IR 1732 and 1709 cm^{-1}, ^1H NMR δ=6.33 (1H, d, J=10 Hz, C_3-H), 6.98 (1H, d, J=10 Hz, C_4-H), 7.27—7.75 (9H, m, C_5-H, C_6-H, C_7-H, and C_3-H, C_4-H, C_5-H of benzoyloxyl groups), 8.08 (4H, dd, J=8 and 2 Hz, C_2-H and C_6-H of benzoyloxyl groups), and 8.18 (1H, bd, J=7.5 Hz, C_8-H). Found: C, 75.00; H, 4.08%. Calcd for $C_{24}H_{16}O_5$: C, 74.99; H, 4.20%.

4-Benzoyloxy-1-naphthol (**22**) (13.3 mg: 2.5%), IR 3580, 3320br, and 1730 cm^{-1}. ^1H NMR δ=6.61 (1H, d, J=8 Hz, C_2-H), 7.07 (1H, d, J=8 Hz, C_3-H), 7.30—7.70 (5H, m, C_6-H, C_7-H, and C_3-H, C_4-H, C_5-H of benzoyloxyl group), ca. 7.81 (1H, m, C_5-H), ca. 8.10 (1H, m, C_8-H), and 8.30 (2H, dd, J=8 and 2 Hz, C_2-H and C_6-H of benzoyloxyl group). Found: C, 77.50; H, 4.40%. Calcd for $C_{17}H_{12}O_3$: C, 77.26; H, 4.58%.

b): **The Condition B.** A solution of **1** (288.0 mg) and benzoyl peroxide (1090.0 mg) in dichloromethane (10 ml) was protected from light and stirred at room temperature for 48 h. After the work-up (as described in *a*)) the crude product was purified by column chromatography on silica gel to give **21** (45.8 mg: 6.0%) and 2-benzoyloxy-1,4-naphthoquinone (**13**) (29.9 mg: 5.3%), mp 118—119 °C (from acetone–hexane), IR 1749 and 1667 cm^{-1}, ^1H NMR δ=6.93 (1H, s, C_3-H), 7.38—7.93 (5H, m, C_6-H, C_7-H, and C_3-H, C_4-H, C_5-H of benzoyloxyl group), ca. 8.11 (2H, m, C_5-H and C_8-H), and 8.18 (2H, dd, J=8 and 2 Hz, C_2-H and C_6-H of benzoyloxyl group). Found: C, 73.59; H, 3.50%. Calcd for $C_{17}H_{10}O_4$: C, 73.38; H, 3.62%.

Oxidation of 2-Naphthol (2) with Benzoyl Peroxide. *a*): A solution of **2** (288.0 mg) and benzoyl peroxide (460.0 mg) in dichloromethane (6.0 ml) was treated under condition A (room temp, 24 h). The crude product was purified by column chromatography on silica gel to give the starting **2** (80.6 mg: 28.0%), a mixture (ca. 1:1) of **4** and **20** (274.0 mg: 51.9%), **21** (57.6 mg: 7.5%), and 1,1-bis(benzoyloxy)-2(1*H*)-naphthalenone (**5**) (21.4 mg: 2.8%), mp 239—240 °C (from acetone), IR 1736 and 1695 cm^{-1}, ^1H NMR δ=6.56 (1H, d, J=10 Hz, C_3-H), 7.26—7.62 (8H, m, C_6-H, C_7-H, and C_3-H, C_4-H, C_5-H of benzoyloxyl groups), 7.50 (1H, d, J=10 Hz, C_4-H), ca. 7.73 (2H, m, C_5-H and C_8-H), and 8.06 (4H, dd, J=8 and 2 Hz, C_2-H and C_6-H of benzoyloxyl groups). Found: C, 75.16; H, 3.97%. Calcd for $C_{24}H_{16}O_5$: C, 74.99; H, 4.20%.

b): A solution of **2** (288.0 mg) and benzoyl peroxide (1090.0 mg) in dichloromethane (10 ml) was treated under condition B (room temp., 48 h). The crude product was purified by column chromatography on silica gel to give **5** (49.1 mg: 6.4%) and **21** (202.6 mg: 26.4%).

c): **The condition of Bhatia and Mathur.**[4] A solution of **2** (1.440 g: 10.0 mmol) and benzoyl peroxide (2.495 g: 10.3 mmol) in chloroform (12.5 ml) was refluxed for 6 h and then treated by the following our method.[17] The reaction mixture was diluted with ether (15 ml), acetic acid (0.5 ml), and aqueous potassium iodide (20%, 20 ml). After stirring at room temperature for 3 h, the mixture was extracted with ether and the ether extract was washed successively with water, aqueous sodium thiosulfate, aqueous sodium hydrogencarbonate, and brine. The dried solution was evaporated in vacuo. The residue was purified by column chromatography on silica gel to give the starting **2** (341 mg: 23.7%), a mixture (ca. 1:1, mp 173—176 °C from chloroform) of **4** and **20** (653 mg: 24.7%), **21** (mp 195—196 °C decomp. from acetone, 287 mg: 7.5%), and **5** (mp 239—240 °C from acetone, 92 mg: 2.4%).

Oxidation of 4-Isopropyl-1-naphthol (18) with Benzoyl Peroxide. *a*): A solution of **18** (372.5 mg) and benzoyl peroxide (460.0 mg) in dichloromethane (6.0 ml) was treated under the condition A (room temp, 24 h). The crude product was chromatographed on silica gel to give five compounds **23**, **24**, **25**, **26**, and **27**.

2-Benzoyloxy-4-isopropyl-1-naphthol (**23**) and 1-benzoyloxy-4-isopropyl-2-naphthol (**24**) in a ratio of ca. 2:3 (258.9 mg: 42.3%), mp 138—142 °C (ca. 2:3 mixture from carbon tetrachloride), IR 3570, 3320br, and 1740 cm^{-1}. Found: C, 78.11; H, 6.01%. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92%. ^1H NMR of **23** δ=1.38 (6H, d, J=7 Hz, -CH(C<u>H</u>$_3$)$_2$), 3.70 (1H, m, -C<u>H</u>(CH$_3$)$_2$), 6.10 (1H, br, C_1-OH), 7.19 (1H, s, C_3-H), 7.33—7.73 (5H, m, C_6-H, C_7-H, and C_3-H, C_4-H, C_5-H of benzoyloxyl group), ca. 8.06 (1H, m, C_5-H), 8.26 (2H, dd, J=8 and 2 Hz, C_2-H and C_6-H of benzoyloxyl group), and 8.31 (1H, m, C_8-H). ^1H NMR of **24** δ=1.38 (6H, d, J=7 Hz -CH(C<u>H</u>$_3$)$_2$), 3.70 (1H, m, -C<u>H</u>(CH$_3$)$_2$), 5.85 (1H, br, C_2-OH), 7.19 (1H, s, C_3-H), 7.33—7.73 (5H, m, C_6-H, C_7-H and C_3-H, C_4-H C_5-H of benzoyloxyl group), 7.84 (1H, m, C_8-H), ca. 8.06 (1H, m, C_5-H), and 8.34 (2H, dd, J=8 and 2 Hz, C_2-H and C_6-H of benzoyloxyl group).

2,2-Bis(benzoyloxy)-4-isopropyl-1(2*H*)-naphthalenone (**25**) (121.1 mg: 14.2%), mp 195—197 °C (from benzene), IR 1727 and 1703 cm^{-1}, ^{1}H NMR δ=1.23 (6H, d, J=7 Hz, -CH(C$\underline{H}_3$)$_2$), 3.17 (1H, m, -C$\underline{H}$(CH$_3$)$_2$), 6.18 (1H, bs, C$_3$-H), 7.30-7.70 (9H, m, C$_5$-H, C$_6$-H, C$_7$-H, and C$_3$-H, C$_4$-H, C$_5$-H of benzoyloxyl groups), 8.06 (4H, dd, J= 8 and 2 Hz, C$_2$-H and C$_6$-H of benzoyloxyl groups), and 8.23 (1H, bd, J=8 Hz, C$_8$-H). Found: C, 75.86; H, 5.43%. Calcd for $C_{27}H_{22}O_5$: C, 76.04; H, 5.20%.

4,4'-Diisopropyl-2,2'-bi-1-naphthol (**26**) (72.0 mg: 6.5%), mp 210—212 °C (from hexane-acetone), MS m/z 370 (M$^+$), IR 3535 and 3270br cm^{-1}, ^{1}H NMR δ=1.41 (12H, d, J=7 Hz, 2-CH(C$\underline{H}_3$)$_2$), 3.72 (2H, m, 2-C$\underline{H}$(CH$_3$)$_2$), 5.56 (2H, bs, 2-OH), 7.32 (2H, bs, C$_3$-H and C$_{3'}$-H), 7.40—7.73 (4H, bm, C$_6$-H, C$_{6'}$-H, C$_7$-H, and C$_{7'}$-H), 7.98—8.27 (2H, bm, C$_5$-H and C$_{5'}$-H), and 8.27—8.53 (2H, bm, C$_8$-H and C$_{8'}$-H). Found: C, 84.54; H, 7.31%. Calcd for $C_{26}H_{26}O_2$: C, 84.29; H, 7.07%. Compound **26** (18.5 mg) was acetylated with acetic anhydride (1.0 ml) in pyridine (1.0 ml) at room temperature for 15 h to give the corresponding diacetate (20.8 mg: 91.5%), mp 166—167 °C (from methanol), IR 1760 cm^{-1}, ^{1}H NMR δ=1.41 (12H, d, J=7 Hz, 2-CH(C$\underline{H}_3$)$_2$), 2.10 (6H, s, 2-OCOC$\underline{H}_3$), 3.77 (2H, m, 2-C$\underline{H}$(CH$_3$)$_2$), 7.43 (2H, s, C$_3$-H and C$_{3'}$-H), 7.47—7.68 (4H, m, C$_6$-H, C$_{6'}$-H, C$_7$-H, and C$_{7'}$-H), 7.72—7.93 (2H, m, C$_8$-H and C$_{8'}$-H), and 8.05—8.28 (2H, m, C$_5$-H and C$_{5'}$-H). Found: C, 78.98; H, 6.71%. Calcd for $C_{30}H_{30}O_4$: C, 79.29; H, 6.65%.

1,1',2,2'-Tetrahydro-4,4'-diisopropyl-1,1'-dioxo-2,2'-binaphthylidene (**27**) (9.8 mg: 1.3%), mp 167—168 °C (from benzene), IR 1629 cm^{-1}, ^{1}H NMR δ=1.36 (12H, d, J=7 Hz, 2-CH(C$\underline{H}_3$)$_2$), 3.26 (2H, m, 2-C$\underline{H}$(CH$_3$)$_2$), 7.27—7.63 (6H, m, C$_5$-H, C$_{5'}$-H, C$_6$-H, C$_{6'}$-H, C$_7$-H, and C$_{7'}$-H), 8.14 (2H, bd, J=8 Hz, C$_8$-H and C$_{8'}$-H), and 8.29 (2H, bs, C$_3$-H and C$_{3'}$-H). Found: C, 84.83; H, 6.49%. Calcd for $C_{26}H_{24}O_2$: C, 84.75; H, 6.57%.

b): A solution of **18** (372.5 mg) and benzoyl peroxide (1090.0 mg) in dichloromethane (10 ml) was treated under condition B (room temp, 48 h). The crude product was chromatographed on silica gel to give a mixture (ca. 2:3) of **23** and **24** (27.0 mg: 4.4%), **25** (557.8 mg: 65.4%), **27** (32.8 mg: 3.1%), and 1,1-bis(benzoyloxy)-4-isopropyl-2(1*H*)-naphthalenone (**28**) (35.8 mg: 4.2%), mp 204—205 °C (from methanol-acetone), IR 1737 and 1680 cm^{-1}, ^{1}H NMR δ=1.41 (6H, d, J=7 Hz, -CH(C$\underline{H}_3$)$_2$), 3.35 (1H, m, -C$\underline{H}$(CH$_3$)$_2$), 6.51 (1H, bs, C$_3$-H), 7.30—7.87 (10H, m, C$_5$-H, C$_6$-H, C$_7$-H, C$_8$-H, and C$_3$-H, C$_4$-H, C$_5$-H of benzoyloxyl groups), and 8.06 (4H, dd, J=8 and 2 Hz, C$_2$-H and C$_6$-H of benzoyloxyl groups). Found: C, 75.82; H, 5.00%. Calcd for $C_{27}H_{22}O_5$: C, 76.04 H, 5.20%.

Oxidation of 3-Isopropyl-2-naphthol (19) with Benzoyl Peroxide. *a*): A solution of **19** (372.5 mg) and benzoyl peroxide (460.0 mg) in dichloromethane (6.0 ml) was treated under condition A (room temp, 24 h). The crude product was chromatographed on silica gel to give the starting **19** (59.5 mg: 16.0%) and three other compounds **29**, **30**, and **31**.

2-Benzoyloxy-3-isopropyl-1-naphthol (**29**) and 1-benzoyloxy-3-isopropyl-2-naphthol (**30**) in a ratio of ca. 1:1 (405.7 mg: 66.2%), IR 3575, 3320br, and 1737 cm^{-1}. The mixture was recrystallized from carbon tetrachloride to give pure **30**, mp 137—138 °C, ^{1}H NMR δ=1.36 (6H, d, J=7 Hz, -CH(C$\underline{H}_3$)$_2$), 3.47 (1H, m, -C$\underline{H}$(CH$_3$)$_2$), 5.76 (1H, bs, C$_2$-OH), 7.27—7.87 (7H, m, C$_5$-H, C$_6$-H, C$_7$-H, C$_8$-H, and C$_3$-H, C$_4$-H, C$_5$-H of benzoyloxyl group), 7.60 (1H, s, C$_4$-H), and 8.34 (2H, dd, J=8 and 2 Hz, C$_2$-H and C$_6$-H of benzoyloxyl group). Found: C, 78.29; H, 5.89%. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92%. ^{1}H NMR of **29** δ=1.32 (6H, d, J=7 Hz, -CH(C$\underline{H}_3$)$_2$), 3.18 (1H, m, -C$\underline{H}$(CH$_3$)$_2$), 5.85 (1H, br, C$_1$-OH), 7.29—7.89 (6H, m, C$_5$-H, C$_6$-H, C$_7$-H, and C$_3$-H, C$_4$-H, C$_5$-H of benzoyloxyl group), 7.38 (1H, s, C$_4$-H), ca. 8.20 (1H, m, C$_8$-H), and 8.26 (2H, dd, J=8 and 2 Hz, C$_2$-H and C$_6$-H of benzoyloxyl group).

2,2-Bis(benzoyloxy)-3-isopropyl-1(2*H*)-naphthalenone (**31**) (72.1 mg: 8.5%), mp 219—220 °C (from acetone), IR 1729 and 1703 cm^{-1}, ^{1}H NMR δ=1.11 (6H, d, J=7 Hz, -CH(C$\underline{H}_3$)$_2$), 2.95 (1H, m, -C$\underline{H}$(CH$_3$)$_2$), 6.88 (1H, bs, C$_4$-H), 7.25—7.73 (9H, m, C$_5$-H, C$_6$-H, C$_7$-H, and C$_3$-H, C$_4$-H, C$_5$-H of benzoyloxyl groups), ca. 8.10 (1H, m, C$_8$-H), and 8.10 (4H, dd, J=8 and 2 Hz, C$_2$-H and C$_6$-H of benzoyloxyl groups). Found: C, 76.20; H, 5.13%. Calcd for $C_{27}H_{22}O_5$: C, 76.04; H, 5.20%.

b): A solution of **19** (372.5 mg) and benzoyl peroxide (1090.0 mg) in dichloromethane (10 ml) was treated under condition B (room temp., 48 h). The crude product was chromatographed on silica gel to give a mixture (ca. 1:1) of **29** and **30** (30.6 mg: 5.0%), **31** (554.4 mg: 65.0%), and 1,1-bis(benzoyloxy)-3-isopropyl-2(1*H*)-naphthalenone (**32**) (122.9 mg: 14.4%), mp 198—199 °C (from acetone), IR 1731 and 1683 cm^{-1}, ^{1}H NMR δ=1.27 (6H, d, J=7 Hz, -CH(C$\underline{H}_3$)$_2$), 3.17 (1H, m, -C$\underline{H}$(CH$_3$)$_2$), 7.18—7.62 (9H, m, C$_5$-H, C$_6$-H, C$_7$-H, and C$_3$-H, C$_4$-H, C$_5$-H of benzoyloxyl groups), 7.23 (1H, bs, C$_4$-H), ca. 7.70 (1H, m, C$_8$-H), and 8.06 (4H, dd, J=8 and 2 Hz, C$_2$-H and C$_6$-H of benzoyloxyl groups). Found: C, 76.06; H, 5.24%. Calcd for $C_{27}H_{22}O_5$: C, 76.04; H, 5.20%.

2-Benzoyloxy-1,4-naphthoquinone (13). *a*): A mixture (ca. 1:1) of **4** and **20** (52.8 mg) was oxidized with Jones reagent (2.5 mol dm^{-3}: 0.24 ml) in acetone (2.0 ml) at 0—5 °C for 15 min. The mixture was diluted with water and extracted with ether. The ether extract was washed with brine, dried, and evaporated in vacuo. The residue was chromatographed on silica gel (5.0 g), using benzene as an eluent, to give a quinone (7.6 mg: 13.7%), the IR and ^{1}H NMR spectra of which were identical with those of **13**.

b): A solution of **21** (38.4 mg), *m*-chloroperbenzoic acid (80%, 25.8 mg), and *p*-toluenesulfonic acid monohydrate (4.0 mg) in dichloromethane (1.0 ml) was refluxed for 2 h. The solution was cooled, diluted with ether, and then washed successively with aqueous potassium iodide, aqueous sodium thiosulfate, aqueous sodium hydrogencarbonate, and brine. The dried solution was evaporated in vacuo. The residue was chromatographed on silica gel (5.0 g), using hexane-benzene (1:1) as an eluent, to give the recovered **21** (14.3 mg) and a quinone (6.0 mg: 21.6%), whose IR and ^{1}H NMR spectra were identical with those of **13**.

Oxidation of 26 with Potassium Hexacyanoferrate(III). A solution of potassium hexacyanoferrate(III) (150.0 mg) in aqueous potassium hydroxide (0.2 mol dm^{-3}, 15.0 ml) was added dropwise to a stirred solution of **26** (24.6 mg) in methanol (5.0 ml) with cooling in an ice-water bath. The mixture was further stirred at room temperature for 15 min. The precipitated product was collected and washed with water. The dried product was recrystallized from benzene to give **27** (20.0 mg: 80.7%), mp 167—168 °C, the IR and ^{1}H NMR spectra of which were identical with those of the

authentic sample.

1-Acetoxy-2-benzoyloxynaphthalene (33) and 2-Acetoxy-1-benzoyloxynaphthalene (34). A mixture (ca. 1:1) of **4** and **20** (63.0 mg) was refluxed with isopropenyl acetate (0.27 ml) and *p*-toluenesulfonic acid monohydrate (3.2 mg) in toluene (0.7 ml) for 3 h. The mixture was cooled, diluted with ether, and washed with aqueous sodium hydrogencarbonate and brine. The dried solution was evaporated in vacuo. The residue was chromatographed on silica gel (10 g), using benzene as an eluent, to give **33** (20.6 mg: 28.0%), mp 144—145 °C (from methanol), IR 1763 and 1740 cm^{-1}, ^1H NMR δ=2.30 (3H, s, $-OCOCH_3$), 7.40—7.95 (7H, m, C_5-H, C_6-H, C_7-H, C_8-H, and C_3-H, C_4-H, C_5-H of benzoyloxyl group), 7.43 (1H, d, J=9 Hz, C_3-H), 7.78 (1H, d, J=9 Hz, C_4-H), and 8.20 (2H, dd, J=8 and 2 Hz, C_2-H and C_6-H of benzoyloxyl group). Found: C, 74.56; H, 4.67%. Calcd for $C_{19}H_{14}O_4$: C, 74.45; H, 4.60%.

Further elution with ether-benzene (1:99) afforded **34** (51.8 mg: 70.5%), mp 99—103 °C (from methanol), IR 1763 and 1740 cm^{-1}, ^1H NMR δ=2.16 (3H, s, $-OCOCH_3$), 7.35 (1H, d, J=9 Hz, C_3-H), 7.40—7.98 (7H, m, C_5-H, C_6-H, C_7-H, C_8-H, and C_3-H, C_4-H, C_5-H of benzoyloxyl group), 7.78 (1H, d, J=9 Hz, C_4-H), and 8.29 (2H, dd, J=8 and 2 Hz, C_2-H and C_6-H of benzoyloxyl group). Found: C, 74.62; H, 4.58%. Calcd for $C_{19}H_{14}O_4$: C, 74.45; H, 4.60%.

1,2,4-Triacetoxynaphthalene (35). *a*): A solution of **21** (76.9 mg) in acetic anhydride (1.0 ml) containing concentrated sulfuric acid (30 mg) was stirred at 50 °C for 2 h. The solution was poured into ice-water and extracted with ether. The ether extract was washed successively with brine, aqueous sodium hydrogencarbonate, and brine. The dried solution was evaporated in vacuo. The residue was chromatographed on silica gel (10 g), using ether-benzene (5:95) as an eluent, to give **35** (44.3 mg: 73.3%), mp 137—138 °C (from methanol), IR 1775 cm^{-1}, ^1H NMR δ=2.31 (3H, s, $-OCOCH_3$), 2.43 (6H, s, 2-$OCOCH_3$), 7.28 (1H, s, C_3-H), 7.43—7.67 (2H, m, C_6-H and C_7-H), and 7.76—7.98 (2H, m, C_5-H and C_8-H). Found: C, 63.63; H, 4.65%. Calcd for $C_{16}H_{14}O_6$: C, 63.57; H, 4.67%.

b): A solution of **5** (19.2 mg) in acetic anhydride (0.25 ml) containing concentrated sulfuric acid (7.5 mg) was stirred at 50 °C for 2 h. After the work-up (as described in *a*)) the crude product was purified by column chromatography on silica gel (5.0 g) to give **35** (13.6 mg: 90.0%), whose IR and ^1H NMR spectra were identical with those of the authentic sample.

Catalytic Hydrogenation of 5 and 21. *a*): A mixture of **5** (76.9 mg) and 5% Rh-Al_2O_3 (23.1 mg) in 1,4-dioxane (1.5 ml) was hydrogenated at room temperature under an atmosphere of hydrogen for 3 h. After the usual work-up, the crude product was chromatographed on silica gel (10 g), using hexane-benzene (1:1) as an eluent, to give an oily 1,1-bis(benzoyloxy)-3,4-dihydro-2(1*H*)-naphthalenone (**36**) (24.6 mg: 31.8%) IR 1727 cm^{-1}, ^1H NMR δ=3.10—3.58 (4H, m, $-CH_2CH_2-$), 7.20—7.62 (9H, m, C_5-H, C_6-H, C_7-H, and C_3-H, C_4-H, C_5-H of benzoyloxyl groups), ca. 7.70 (1H, m, C_8-H), and 8.07 (4H, dd, J=8 and 2 Hz, C_2-H and C_6-H of benzoyloxyl groups), MS m/z 386 (M^+). Further elution with benzene afforded a mixture of **4** and **20** (34.6 mg: 65.5%), the IR and ^1H NMR spectra of which were identical with those of the authentic mixture.

b): A mixture of **21** (76.9 mg) and 5% Rh-Al_2O_3 (23.1 mg) in 1,4-dioxane (1.5 ml) was hydrogenated as described in *a*). The crude product was chromatographed on silica gel (10 g), using benzene as an eluent, to give an oily 2,2-bis(benzoyloxy)-3,4-dihydro-1(2*H*)-naphthalenone (**37**) (46.3 mg: 60.0%), IR 1735 and 1710 cm^{-1}, ^1H NMR δ=3.00—3.44 (4H, m, $-CH_2CH_2-$), 7.18—7.86 (9H, m, C_5-H, C_6-H, C_7-H, and C_3-H, C_4-H, C_5-H of benzoyloxyl groups), 8.06 (4H, dd, J=8 and 2 Hz, C_2-H and C_6-H of benzoyloxyl groups), and ca. 8.17 (1H, m, C_8-H), MS m/z 386 (M^+). Further elution with benzene afforded a mixture of **4** and **20** (20.1 mg: 38.0%), the IR and ^1H NMR spectra of which were identical with those of the authentic mixture.

2-Acetoxy-1-benzoyloxy-4-isopropylnaphthalene (38). A mixture (ca. 2:3) of **23** and **24** (66.8 mg) was refluxed with isopropenyl acetate (0.24 ml) and *p*-toluenesulfonic acid monohydrate (3.4 mg) in toluene (1.3 ml) for 5 h. After the work-up (as described above) the crude product was chromatographed on silica gel (10 g), using ether-benzene (1:99) as an eluent, to give **38** (49.2 mg: 64.2%), mp 142—143 °C (from methanol), IR 1769 and 1744 cm^{-1}, ^1H NMR δ=1.41 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 2.17 (3H, s, $-OCOCH_3$), 3.75 (1H, m, $-C\underline{H}(CH_3)_2$), 7.25 (1H, s, C_3-H), 7.30—7.71 (5H, m, C_6-H, C_7-H, and C_3-H, C_4-H, C_5-H of benzoyloxyl group), ca. 7.90 (1H, m, C_8-H), ca. 8.12 (1H, m, C_5-H), and 8.28 (2H, dd, J=8 and 2 Hz, C_2-H and C_6-H of benzoyloxyl group). Found: C, 76.13; H, 6.04%. Calcd for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79%.

The acetate **38** (10.2 mg) was refluxed with dilute hydrochloric acid (15%, 0.1 ml) in methanol (0.9 ml) for 1 h. The mixture was diluted with brine and extracted with ether. The ether extract was washed with brine, dried, and evaporated in vacuo to give **24** (8.7 mg) containing a small amount of **23** (by ^1H NMR analysis). This was dissolved in deuteriochloroform and then allowed to stand at room temperature for 24 h to give an equilibrium mixture of **23** and **24** (ca 2:3).[13]

1-Acetoxy-2-benzoyloxy-3-isopropylnaphthalene (39) and 2-Benzoyloxy-3-isopropyl-1,4-naphthoquinone (40). *a*): A mixture (ca. 1:1) of **29** and **30** (91.2 mg) was refluxed with isopropenyl acetate (0.33 ml) and *p*-toluenesulfonic acid monohydrate (4.6 mg) in toluene (0.9 ml) for 5 h. After the work-up (as described above) the crude product was chromatographed on silica gel (0.040—0.063 mm, 15 g), using hexane-benzene (6:4) as an eluent, to give **40** (20.6 mg: 21.6%), mp 123—125 °C (from hexane), IR 1743 and 1672 cm^{-1}, ^1H NMR δ=1.32 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 3.43 (1H, m, $-C\underline{H}(CH_3)_2$), 7.42—7.87 (5H, m, C_6-H, C_7-H, and C_3-H, C_4-H, C_5-H of benzoyloxyl group), ca. 8.12 (2H, m, C_5-H and C_8-H), and 8.20 (2H, dd, J=8 and 2 Hz, C_2-H and C_6-H of benzoyloxyl group). Found: C, 75.01; H, 5.13%. Calcd for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03%.

Further elution with hexane-benzene (25:75) afforded **39** (78.7 mg: 75.9%), mp 161—164 °C (from methanol), IR 1773 and 1741 cm^{-1}, ^1H NMR δ=1.32 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 2.18 (3H, s, $-OCOCH_3$), 3.19 (1H, m, $-C\underline{H}(CH_3)_2$), 7.32-7.90 (7H, m, C_5-H, C_6-H, C_7-H, C_8-H, and C_3-H, C_4-H, C_5-H of benzoyloxyl group), 7.71 (1H, s, C_4-H), and 8.25 (2H, dd, J=8 and 2 Hz, C_2-H and C_6-H of benzoyloxyl group). Found: 75.70; H, 5.88%. Calcd for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79%.

The acetate **39** (10.5 mg) was refluxed with dilute hydrochloric acid (15%, 0.1 ml) in methanol (0.9 ml) for 1 h.

The mixture was diluted with brine and extracted with ether. The ether extract was washed with brine, dried, and evaporated in vacuo to give **29** (8.5 mg) containing a small amount of **30** (by ^{1}H NMR analysis). This was dissolved in deuteriochloroform and then allowed to stand at room temperature for 24 h to afford an equilibrium mixture of **29** and **30** (ca. 1:1).[13]

b): A solution of **30** (31.6 mg) in acetone (1.0 ml) was oxidized with Jones reagent (2.5 mol dm^{-3}: 0.12 ml) at 0—5 °C for 20 min. After the work-up (as described above) the crude product was chromatographed on silica gel (5.0 g), using hexane–benzene (1:1) as an eluent, to give **40** (10.4 mg: 31.5%), mp 123—125 °C, whose IR and ^{1}H NMR spectra were identical with those of the authentic sample.

c): A solution of **31** (21.3 mg), *m*-chloroperbenzoic acid (80%, 12.9 mg), and *p*-toluenesulfonic acid monohydrate (3.0 mg) in dichloromethane (0.5 ml) was refluxed for 8 h. After the work-up (as described above) the crude product was chromatographed on silica gel (5.0 g), using benzene as an eluent, to give **40** (5.7 mg: 35.6%), mp 123—125 °C, the IR and ^{1}H NMR spectra of which were identical with those of the authentic sample.

1,2,4-Triacetoxy-3-isopropylnaphthalene (41). *a*): A solution of **31** (85.2 mg) and concentrated sulfuric acid (30 mg) in acetic anhydride (1.0 ml) was stirred at 50 °C for 2 h. After the work-up (as described above) the crude product was chromatographed on silica gel (15 g), using ether–benzene (1:99 and then 3:97) as eluents, to give **41** (59.2 mg: 86.0%), mp 152—153 °C (from methanol), IR 1772 cm^{-1}, ^{1}H NMR δ=1.30 (6H, d, J=7 Hz, -CH(C$\underline{H}_3$)$_2$), 2.34 (3H, s), 2.39 (3H, s), and 2.46 (3H, s) (3-OCOC$\underline{H}_3$), 3.24 (1H, m, -C$\underline{H}$(CH$_3$)$_2$), and 7.36—7.80 (4H, m, C$_5$-H, C$_6$-H, C$_7$-H, and C$_8$-H). Found: C, 66.29; H, 6.05%. Calcd for $C_{19}H_{20}O_6$: C, 66.27; H, 5.85%.

b): A solution of **32** (42.5 mg) and concentrated sulfuric acid (15 mg) in acetic anhydride (0.5 ml) was treated as described in *a*). The crude product was chromatographed on silica gel (5.0 g) to give **41** (28.4 mg: 82.8%), mp 152—153 °C, the IR and ^{1}H NMR spectra of which were identical with those of the authentic sample.

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