The Photochemical Reaction of 1,2-Naphthoquinones with Aldehydes. II.[1] The Photo-addition Reactions of Aliphatic Aldehydes to 1,2-Naphthoquinones

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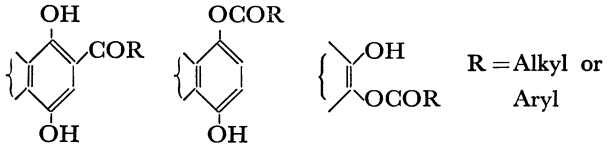
3-Acyl-1,2-naphthalenediols and 1,2-naphthalenediol monoacyl esters were obtained from the photochemical reactions of 1,2-naphthoquinones with aliphatic aldehydes. 3-Halogeno-1,2-naphthoquinones gave the corresponding 1,2-naphthalenediol monoacyl esters, 3-acyl-1,2-naphthalenediols, which are the same products as those from the photochemical reactions of 1,2-naphthoquinone with those aldehydes and 3-halogeno-4-acyl-1,2-naphthoquinone when they were irradiated in aldehydes. 3-Methyl-1,2-naphthoquinone, however, gave the corresponding 1,2-naphthalenediol monoacetate and 3-methyl-4-acetyl-1,2-naphthoquinone when it was irradiated in acetaldehyde. These photochemical reactions were applicable for syntheses of 3-acyl-1,2-naphthalenediols and 1,2-naphthalenediol monoacyl esters.

The wide variety of photo-induced reactions among quinones and aldehydes has been examined by several workers.[2] The photochemical reactions of *p*-benzoquinones and 1,4-naphthoquinones with aliphatic or aromatic aldehydes give acyl or aroylquinols (**1**) and quinol monoesters (**2**).

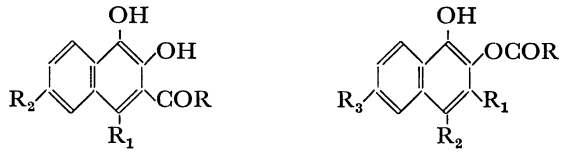


1 **2** **3**

On the other hand, *o*-quinones usually give the corresponding enediol monoesters (**3**) exclusively. For example, tetrachloro-1,2-benzoquinone yields tetrachlorocatechol monoacetate and monobenzoate when it is irradiated in the presence of acetaldehyde and benzaldehyde.[3] 9,10-Phenanthrenequinone reacts in a similar fashion with both aliphatic or aromatic aldehydes.[4] 4-Cyano-1,2-naphthoquinone, however, behaves differently, since with aromatic aldehydes it gives naphthalenediol monoesters, but the products from the reaction with acetaldehyde and propionaldehyde are reported to be the corresponding 1,2-dihydroxy-3-acyl-4-naphthalenecarbonitriles.[5] But no factor leading to monoesters of 1,2-naphthalenediol or to ring-acylated 1,2-naphthalenediols has been discovered yet. Therefore, it is necessary to scrutinize the photochemical reactions of 1,2-naphthoquinones with aliphatic aldehydes. In this work, the photochemical reactions of 1,2-naphthoquinone and its derivatives with a variety of aliphatic aldehydes were examined. It was found that 3-acyl-1,2-naphthalenediols and 1,2-naphthalenediol monoacyl esters were usually obtained with the exception of the cases in which the 3-position of a quinone ring was substituted.

Results and Discussion

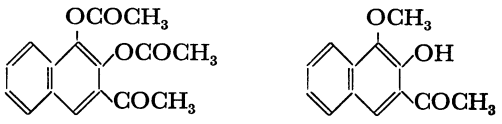
The 1,2-naphthoquinones examined in this work are 1,2-naphthoquinone and its 3-chloro-, 3-bromo-, 3-methyl-, 4-cyano-, 6-bromo-, and 6-methyl-derivatives. The aldehydes used are acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, valeraldehyde, isovaleraldehyde, hexanal, heptanal, octanal nonanal, and decanal.



4 **5**

$R=CH_3(CH_2)_n$ ($n=0$—8)

A benzene solution of 1,2-naphthoquinones and an aldehyde was irradiated by means of a 300-W high pressure Hg arc lamp through a 5 cm thick layer of flowing water. The structures of the photo-addition compounds were determined by the following procedures. As a typical example, the photochemical reaction of 1,2-naphthoquinone with acetaldehyde will be illustrated. After the usual work-up of the reaction mixture, orange colored prisms (**4a**: $R=CH_3$, $R_1=R_2=H$; 24%) and white crystals (**5a**: $R=CH_3$, $R_1=R_2=R_3=H$; 39%) were obtained. The compound, **4a**, has carbonyl (1652 cm^{-1}) and hydroxyl (3400 cm^{-1}) groups, judging from its infrared spectrum. The PMR of **4a** showed signals at δ: 2.76 (s, 3H, $COCH_3$), 5.91 (s, 1H), 7.18—8.08 (m, 5H, aromatic protons), and 11.48 (s, 1H). The signal at δ: 5.91 and 11.48 disappeared after shaking with deuterium oxide, so these two signals could be assigned to the hydroxyl groups. The signal which appears at δ: 11.48 should be assigned to the 2-hydroxyl group, which is intramolecularly hydrogen-bonded to the adjacent carbonyl of the neighboring acetyl group.



6 **7**

The acetylated or methylated derivatives were confirmed to be **6** and **7** by their IR and PMR analyses. From these results the orange-colored photo-addition compound should have structure **4a**. Such photo-addition compounds are colored yellow to orange. The IR of another white photo-adduct (**5a**) showed absorption bands at 3400 and 1743 cm^{-1}, corresponding to hydroxyl and carbonyl groups respectively. The white crystal was the nearly 1 : 1 mixture of two isomeric esters, since two sorts of methyl proton signals of acetoxyl

groups were observed at δ: 2.42 and 2.52 by PMR analysis.

3-Acyl-1,2-naphthalenediols and 1,2-naphthalenediol monoacyl esters were also obtained from the photochemical reactions of nonsubstituted 1,2-naphthoquinone, 4-cyano-, 6-bromo-, and 6-methyl-derivatives of 1,2-naphthoquinone with aliphatic aldehydes. Awad and Hafez have reported that when a strong electron attracting group such as the cyano group was introduced at position 4 of 1,2-naphthoquinone, 3-acylated 1,2-naphthalenediols were the products in the photochemical reactions with acetaldehyde or propionaldehyde.[6] Since 3-acylated 1,2-naphthalenediols were also obtained from the photochemical reactions of 1,2-naphthoquinone with aliphatic aldehydes, it is of interest to investigate the role of the cyano group in the reaction.

Photochemical reactions of 3-substituted 1,2-naphthoquinones, such as 3-chloro-, 3-bromo-, and 3-methyl-1,2-naphthoquinone, with aliphatic aldehydes were chosen for this purpose. Irradiation of 3-halogeno-1,2-naphthoquinone in acetaldehyde afforded, however, 3-halogeno-1,2-naphthalenediol monoacetates (**5**: R=CH_3, R_1=Cl or Br, R_2=R_3=H, 26%) as the main products, plus paraldehyde (*ca.* 90%) along with a little metaldehyde. The use of benzene as a solvent did not interfere with these photochemical reactions. Polymerization of acetaldehyde suggested that a hydrogen halide had been formed in the reaction system.

In view of these results, a detailed analysis of the minor products in these reactions was required. In fact, 3-acetyl-1,2-naphthalenediol (1—3%), which is the same product as in the photochemical reaction of 1,2-naphthoquinone with acetaldehyde, and 3-halogeno-4-acetyl-1,2-naphthoquinone (2—5%) were isolated. 3-Chloro-4-acetyl-1,2-naphthoquinone was identified by comparison with the authentic sample prepared by the chlorination of 4-acetyl-1,2-naphthoquinone. Analogous products were also obtained from the photochemical reactions of 3-halogeno-1,2-naphthoquinone with other aliphatic aldehydes. Irradiation of a benzene solution of 3-methyl-1,2-naphthoquinone and acetaldehyde gave 3-methyl-1,2-naphthalenediol monoacetate (17.7%) and 3-methyl-4-acetyl-1,2-naphthoquinone (6.6%). It is thought that 3-halogeno-4-acetyl-1,2-naphthalenediols and 3-methyl-4-acetyl-1,2-naphthalenediol converted into the corresponding quinones by oxidation with the original quinone in the reaction system or with air during the separation procedure, since 3-chloro-4-acetyl-1,2-naphthalenediol was easily auto-oxidized into 3-chloro-4-acetyl-1,2-naphthoquinone in silica gel or in benzene solution.

Even after a benzene solution of 1,2-naphthalenediol monoacetate [**5a**; λ_{max} (ε): 329 nm (2310)] was irradiated for 1—3 days, no 3-acetyl-1,2-naphthalenediol (**4a**) was detected by PMR analysis. However, the rearrangement of **5a** to **4a** might be sensitized by 1,2-naphthoquinone. This possibility was checked by irradiating a mixture of 1,2-naphthoquinone and **5a** in benzene, but no **4a** was detected. Therefore, under these conditions the photo-induced Fries rearrangement of **5a** to **4a** is unlikely. The detailed mechanism of the formation of these photo-adducts remains still unestablished, but the results examined so far have been described in this paper as a preliminary report.

Experimental

All melting points were determined on a Yanagimoto Micro-melting Point apparatus and are uncorrected. Yields were based on the amount of quinones used. PMR spectra were taken with a JEOL MH-100 spectrometer in CCl_4 or $CDCl_3$ solution using TMS as the internal standard. The coupling constants were 7.0—8.0 Hz in all compounds. Infrared spectra were obtained on a Hitachi 215 spectrometer, using a KBr disc. Ultraviolet spectra were recorded by means of a Hitachi 124 spectrophotometer.

Materials. 1,2-naphthoquinone (mp 121—122 °C) was prepared by the oxidation of 1-amino-2-naphthol hydrochloride with iron(III) chloride.[7] 3-Chloro (mp 171 °C)[8] and 3-bromo-1,2-naphthoquinone (mp 164 °C)[9] were prepared by chlorination or bromination of 1,2-naphthoquinone. 3-Methyl-1,2-naphthoquinone (mp 120 °C) was prepared by the oxidation of 3-methyl-α-tetralone with selenium dioxide.[10] 4-Cyano-1,2-naphthoquinone (mp 175—176 °C) was prepared by the oxidation of 1-amino-2-hydroxy-4-cyanonaphthalene with chromium trioxide.[11] 6-Bromo-1,2-naphthoquinone (mp 156 °C) was prepared by the oxidation of 6-bromo-2-naphthol with Fremy's salt.[12] 6-Methyl-1,2-naphthoquinone (mp 126—127 °C) was prepared by the oxidation of 6-methyl-2-naphthol with Fremy's salt at 15 °C.[14] All commercially available aldehydes were further purified by distillation under nitrogen.

General Procedures. A typical photochemical reaction was performed as follows: 1,2-naphthoquinone derivatives (200 mg, 0.84—1.27 mmol) and aldehydes (500 mg, 3—11 mmol) were dissolved in 25 ml of benzene, and the solution was irradiated from outside in an ordinary tube by a 300 W high-pressure mercury arc lamp through a 5 cm thick layer of flowing water at 15—20 °C. After 2—10 days, the characteristic color of 1,2-naphthoquinones faded to yellow. Benzene was removed under reduced pressure, and then the residue was chromatographed on silica gel, using benzene as the eluting solvent. Appropriate fractions were collected and concentrated and then light petroleum was added; these gave photo-adducts. The photo-adducts were further purified by recrystallization from benzene or benzene-light petroleum or by a florisil column.

Photo-addition Products of 1,2-Naphthoquinone with Aliphatic Aldehyde. (i) Acetaldehyde: 3-Acetyl-1,2-naphthalenediol [**4a**: R=CH_3, R_1=R_2=H]: orange prisms (60 mg, 24%), mp 135—136 °C. IR: ν_{OH} 3440; $\nu_{C=O}$ 1652 cm^{-1}. PMR (CCl_4), δ: 2.76 (s, 3H, CH_3), 5.91 (s, 1H, OH, removed by D_2O), 7.17—8.08 (m, 5H, aromatic-H), 11.48 (s, 1H, OH, removed by D_2O). UV($CHCl_3$): λ_{max} (ε), 409 (7330), 300(21500), 263(38500). Found: C, 71.07; H, 4.49%. Calcd for $C_{13}H_{10}O_3$: C, 71.28; H, 4.98%. Treatment with acetic anhydride afforded 3-acetyl-1,2-naphthalenediol diacetate (**6**): pale yellow crystals from ethanol, mp 155–157 °C. IR: $\nu_{C=O}$ 1770, 1687 cm^{-1}. PMR($CDCl_3$), δ: 2.37(s, 3H, $OCOCH_3$), 2.46 (s, 3H, $OCOCH_3$), 2.67(s, 3H, $COCH_3$), 7.28—8.18 (m, 5H, aromatic-H). Treatment with dimethylsulfate in aqueous sodium hydroxide afforded 1-methoxy-2-hydroxy-3-acetylnaphthalene (**7**): yellow crystals, mp 80—81 °C. IR: ν_{OH} 3420; $\nu_{C=O}$ 1655 cm^{-1}. PMR(CCl_4), δ: 2.78(s, 3H, $COCH_3$), 4.06(s, 3H, OCH_3), 7.16—8.05 (m, 5H, aromatic-H), 11.42(s, 1H, OH, removed by D_2O). 1,2-Naphthalenediol monoacetate [**5a**: R=CH_3, R_1=R_2=R_3=H]: white crystals (100 mg, 39%), mp 136—138 °C. IR: ν_{OH} 3400; $\nu_{C=O}$ 1740 cm^{-1}. PMR($CDCl_3$), δ: 2.40(s, 3H, CH_3),

2.52(s, 3H, CH_3), 7.13—7.88(m, 14H, aromatic-H+OH). UV($CHCl_3$): $\lambda_{max}(\varepsilon)$, 329(2310), 288(4960), 278 nm (6090). Found: C, 70.98; H, 4.76%. Calcd for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98%. Treatment with acetic anhydride afforded 1,2-naphthalenediol diacetate: white crystals, mp 108—111 °C. It was identified (mixed melting point, IR and PMR spectra) by comparison with an authentic sample.

(ii) Propionaldehyde: 3-Propionyl-1,2-naphthalenediol [**4**: $R=CH_3CH_2, R_1=R_2=H$]: orange yellow prisms (51mg,19%), mp 129—130.5 °C. IR: ν_{OH} 3455; $\nu_{C=O}$ 1660 cm^{-1}. PMR (CCl_4), δ: 1.32 (t, 3H, CH_3), 3.20 (q, 2H, CH_2), 5.93 (s, 1H, OH, removed by D_2O), 7.16—8.11 (m, 5H, aromatic-H), 11.57 (s, 1H, OH, removed by D_2O). Found: C, 72.36; H, 5.62%. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59%. 1,2-Naphthalenediol monopropionate [**5**: $R=CH_3CH_2, R_1=R_2=R_3=H$]: white crystals (38 mg, 14%), mp 105—106 °C. IR: ν_{OH} 3440; $\nu_{C=O}$ 1750 cm^{-1}. PMR($CDCl_3$), δ: 1.32 (t, 3H, CH_3), 1.42 (t, 3H, CH_3), 2.72(q, 2H, CH_2), 2.84 (q, 2H, CH_2), 7.10—7.83(m, 14H, aromatic-H+OH). Found: C, 72.15; H, 5.80%. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59%.

(iii) Butyraldehyde: 3-Butyryl-1,2-naphthalenediol [**4**: $R=CH_3(CH_2)_2$, $R_1=R_2=H$]: orange prisms (59 mg, 20%), mp 98.0—99.5 °C. IR: ν_{OH} 3455; ν_{CH} 2980; $\nu_{C=O}$ 1655 cm^{-1}. PMR(CCl_4), δ: 1.06(t, 3H, CH_3), 1.82(sex, 2H, CH_2), 3.06 (t, 2H, $COCH_2$), 5.84 (s, 1H, OH), 7.06—7.98(m, 5H, aromatic-H), 11.45(s, 1H, OH). Found: C, 72.94; H, 6.02%. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13%. 1,2-Naphthalenediol monobutyrate [**5**: $R=CH_3(CH_2)_2$, $R_1=R_2=R_3=H$]: white crystals (21 mg, 7%), mp 77—78 °C. IR: ν_{OH} 3320; ν_{CH} 2980; $\nu_{C=O}$ 1725 cm^{-1}. PMR($CDCl_3$), δ: 1.08 (t, 3H, CH_3), 1.88 (sex, 2H, CH_2), 2.64 (t, 2H, $COCH_2$), 7.08—8.10 (m, 7H, aromatic-H+OH). Found: C, 73.58; H, 6.35%. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13%.

(iv) Isobutyraldehyde: 3-Isobutyryl-1,2-naphthalenediol [**4**: $R=(CH_3)_2CH$, $R_1=R_2=H$]: yellow crystals (15 mg, 5%), mp 105—107 °C. IR: ν_{OH} 3500; ν_{CH} 2985, 2950; $\nu_{C=O}$ 1655 cm^{-1}. PMR (CCl_4), δ: 1.30 (d, 6H, $(CH_3)_2$), 3.77 (sep, 1H, CH), 5.97(s, 1H, OH), 7.12—8.12 (m, 5H, aromatic-H), 11.80 (s, 1H, OH). Found: C, 72.81; H, 6.21%. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13%. 1,2-Naphthalenediol monoisobutyrate [**5**: $R=(CH_3)_2CH$, $R_1=R_2=R_3=H$]: white crystals (80 mg, 27.5%), mp 73—74 °C. IR: ν_{OH} 3350 (br), ν_{CH} 2955; $\nu_{C=O}$ 1742, 1725 cm^{-1}. PMR($CDCl_3$), δ: 1.37(d, 6H, $(CH_3)_2$), 1.46(d, 6H, $(CH_3)_2$), 2.78 (sep, 1H, CH), 3.00(sep, 1H, CH), 7.13—8.30 (m, 14H, aromatic-H+OH). Found: C, 72.83; H, 5.96%. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13%.

(v) Valeraldehyde: 3-Valeryl-1,2-naphthalenediol (**4**: $R=CH_3(CH_2)_3, R_1=R_2=H$]: orange yellow prisms (25mg, 8.1%), mp 131—132 °C. IR: ν_{OH} 3455; ν_{CH} 2970; $\nu_{C=O}$ 1645 cm^{-1}. PMR(CCl_4), δ: 0.98 (t, 3H, CH_3), 1.24—1.88(m, 4H, $(CH_2)_2$), 3.05 (t, 2H, $COCH_2$), 5.92 (s, 1H, OH), 7.13—8.05 (m, 5H, aromatic-H), 11.44(s, 1H, OH). Found: C, 73.53; H, 6.71%. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60%. 1,2-Naphthalenediol monovalerate [**5**: $R=CH_3(CH_2)_3$, $R_1=R_2=R_3=H$]: white crystals (48 mg, 15.5%), mp 68.5—71.0 °C. IR: ν_{OH} 3410; ν_{CH} 2960, 2940; $\nu_{C=O}$ 1735 cm^{-1}. PMR (CCl_4), δ: 0.98 (t, 3H, CH_3), 1.29—1.94 (m, 4H, $(CH_2)_2$), 2.47 (t, 2H, $COCH_2$), 6.17(1H, OH, broad), 6.87—7.67 (m, 6H, aromatic-H). Found: C, 74.00; H, 6.48%. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60%.

(vi) Isovaleraldehyde: 3-Isovaleryl-1,2-naphthalenediol [**4**: $R=(CH_3)_2CHCH_2$, $R_1=R_2=H$]: orange yellow oil (23 mg, 8%). PMR(CCl_4), δ: 1.00(d, 6H, $(CH_3)_2$), 2.30(m, 1H, CH), 2.89(d, 2H, $COCH_2$), 5.85 (s, 1H, OH), 7.08—8.05 (m, 5H, aromatic-H), 11.67 (s, 1H, OH). 1,2-Naphthalenediol monoisovalerate [**5**: $R=(CH_3)_2CHCH_2$, $R_1=R_2=R_3=H$]:white crystals (50 mg, 16%), mp 79.0—81.5 °C. IR: ν_{OH} 3420; ν_{CH} 2960, 2940, 2875; $\nu_{C=O}$ 1735, 1725 cm^{-1}. PMR (CCl_4), δ: 1.05 (d, 6H, $(CH_3)_2$), 1.09 (d, 6H, $(CH_3)_2$), 2.10—2.45(m, 2H, CH), 2.42(d, 2H, $COCH_2$), 2.56(d, 2H, $COCH_2$), 6.06(OH, 2H, broad), 6.90—8.18(m, 10H, aromatic-H). Found: C, 73.28; H, 6.81%. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60%.

(vii) Hexanal: 3-Hexanoyl-1,2-naphthalenediol [**4**: $R=CH_3(CH_2)_4$, $R_1=R_2=H$]: orange yellow prisms (40 mg, 12.3%), mp 119—120 °C. IR: ν_{OH} 3450; ν_{CH} 2935, 2870; $\nu_{C=O}$ 1645 cm^{-1}. PMR ($CDCl_3$), δ: 0.80—1.95 (m, 9H, $CH_3(CH_2)_3$), 3.07 (t, 2H, $COCH_2$), 5.97 (s, 1H, OH), 7.20—8.02 (m, 5H, aromatic-H), 11.60 (s, 1H, OH). Found: C, 74.31; H, 6.95%. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02%. 1,2-Naphthalenediol monohexanoate [**5**: $R=CH_3(CH_2)_4$, $R_1=R_2=R_3=H$]: white crystals (40 mg, 12.3%), mp 79.0—81.5 °C. IR: ν_{OH} 3410; ν_{CH} 2960, 2935, 2870; $\nu_{C=O}$ 1735 cm^{-1}. PMR($CDCl_3$), δ: 0.83—1.90 (m, 18H, $CH_3(CH_2)_3$), 2.57 (t, 2H, $COCH_2$), 2.70(t, 2H, $COCH_2$), 6.90—7.70 (m, 12H, aromatic-H+OH). Found; C, 74.56; H, 7.20%. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02%.

(viii) Heptanal: 3-Heptanoyl-1,2-naphthalenediol [**4**: $R=CH_3(CH_2)_5$, $R_1=R_2=H$]: yellow plates (35 mg, 10.2%), mp 105—106 °C. IR: ν_{OH} 3470; ν_{CH} 2975, 2945, 2855; $\nu_{C=O}$ 1645 cm^{-1}. PMR(CCl_4), δ: 0.92 (t, 3H, CH_3), 1.23—1.90 (m, 8H, $(CH_2)_4$), 3.04(t, 2H, $COCH_2$), 5.95 (s, 1H, OH), 7.13—8.07 (m, 5H, aromatic-H), 11.65 (s, 1H, OH). Found: C, 74.77; H, 7.30%. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40%. 1,2-Naphthalenediol monoheptanoate [**5**: $R=CH_3(CH_2)_5$, $R_1=R_2=R_3=H$]: white needles (65 mg, 19%), mp 59 °C. IR: ν_{OH} 3460; ν_{CH} 2950, 2870; $\nu_{C=O}$ 1760, 1740 cm^{-1}. PMR(CCl_4), δ: 0.80—1.96 (m, 22H, $CH_3(CH_2)_4$), 2.64 (t, 2H, $COCH_2$), 2.76 (t, 2H, $COCH_2$), 7.12—8.32 (m, 14H, aromatic-H+OH). Found: C, 75.15; H, 7.47%. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40%.

(ix) Octanal: 3-Octanoyl-1,2-naphthalenediol [**4**: $R=CH_3(CH_2)_6$, $R_1=R_2=H$]: orange prisms (40 mg, 14%), mp 98—99 °C. IR: ν_{OH} 3460; ν_{CH} 2945, 2872; $\nu_{C=O}$ 1650 cm^{-1}. PMR(CCl_4), δ: 0.90 (t, 3H, CH_3), 1.22—1.89 (m, 10H, $(CH_2)_5$), 3.05(t, 2H, $COCH_2$), 5.98 (s, 1H, OH), 7.11—8.04 (m, 5H, aromatic-H), 11.72(s, 1H, OH). Found: C, 75.32; H, 7.64%. Calcd for $C_{18}H_{22}O_3$: C, 75.50; H, 7.74%. 1,2-Naphthalenediol monooctanoate [**5**: $R=CH_3(CH_2)_6$, $R_1=R_2=R_3=H$]: white plates (75 mg, 26.2%), mp 53—54 °C. IR: ν_{OH} 3340; ν_{CH} 2920, 2855; $\nu_{C=O}$ 1755, 1735 cm^{-1}. PMR (CCl_4), δ: 0.82—1.82 (m, 26H, $CH_3(CH_2)_5$), 2.50 (t, 2H, $COCH_2$), 2.62 (t, 2H, $COCH_2$), 6.12 (2H, OH), 6.98—8.16 (m, 12H, aromatic-H). Found: C, 75.66; H, 7.70%. Calcd for $C_{18}H_{22}O_3$: C, 75.50; H, 7.74%.

(x) Nonanal: 3-Nonanoyl-1,2-naphthalenediol [**4**: $R=CH_3(CH_2)_7$, $R_1=R_2=H$]: yellowish orange prisms (38 mg, 10%), mp 99—100 °C. IR: ν_{OH} 3475; ν_{CH} 2975, 2945, 2855; $\nu_{C=O}$ 1647 cm^{-1}. PMR(CCl_4), δ: 0.87 (t, 3H, CH_3), 1.18—1.90 (m, 12H, $(CH_2)_6$), 3.06 (t, 2H, $COCH_2$), 5.91 (s, 1H, OH), 7.14—8.07 (m, 5H, aromatic-H), 11.64 (s, 1H, OH). Found: C, 75.63; H, 7.81%. Calcd for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05%. 1,2-Naphthalenediol monononanoate [**5**: $R=CH_3(CH_2)_7$, $R_1=R_2=R_3=H$]: white needles (62 mg, 16.4 %), mp 62.5—63.5 °C. IR: ν_{OH} 3400, ν_{CH} 2935, 2863; $\nu_{C=O}$ 1730 cm^{-1}. PMR (CCl_4), δ: 0.80—1.90 (m, 15H, $CH_3(CH_2)_6$), 2.77 (t, 2H, $COCH_2$), 7.12—7.84 (m, 7H, aromatic-H+OH). Found: C, 76.08; H, 7.94%. Calcd for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05%.

(xi) Decanal: 3-Decanoyl-1,2-naphthalenediol [**4**: $R=CH_3(CH_2)_8$, $R_1=R_2=H$]: orange prisms (34 mg, 8.6 %), mp 88—89 °C. IR: ν_{OH} 3465; ν_{CH} 2945, 2857; $\nu_{C=O}$ 1648 cm^{-1}.

PMR(CCl_4), δ: 0.87 (t, 3H, CH_3), 1.15—1.89 (m, 14H, $(CH_2)_7$), 5.90 (s, 1H, OH), 7.14—8.06 (m, 5H, aromatic-H), 11.64 (s, 1H, OH). Found: C, 76.37; H, 8.27%. Calcd for $C_{20}H_{26}O_3$: C, 76.40; H, 8.33%. 1,2-Naphthalenediol monodecanoate [**5**: $R=CH_3(CH_2)_8$, $R_1=R_2=R_3=H$]: white needles (61 mg, 15.4%), mp 67—68 °C. IR: ν_{OH} 3385; ν_{CH} 2935, 2860; $\nu_{C=O}$ 1729 cm^{-1}. PMR (CCl_4), δ: 0.86—1.82 (m, 17H, $CH_3(CH_2)_7$), 2.85 (t, 2H, $COCH_2$), 7.08—7.80 (m, 7H, aromatic-H+OH). Found: C, 76.67; H, 8.42%. Calcd for $C_{20}H_{26}O_3$: C, 76.40; H. 8.33%.

Photo-addition Compounds of 4-Cyano-1,2-naphthoquinone with Aliphatic Aldehyde. *(i) Acetaldehyde*: 1,2-Dihydroxy-3-acetyl-4-naphthalenecarbonitrile [**4**: $R=CH_3$, $R_1=CN$, $R_2=H$]: orange yellow needles (56 mg, 22.5%), mp 213—217 °C. IR: ν_{OH} 3435; ν_{CN} 2225; $\nu_{C=O}$ 1640 cm^{-1}. PMR ($CDCl_3$), δ: 3.17 (s, 3H, CH_3), 6.73 (s, 1H, OH, removed by D_2O), 7.52—7.77, 8.10—8.52 (m, 4H, aromatic-H), 12.03 (s, 1H, OH, removed by D_2O). Found: C, 69.04; H, 3.99; N, 5.98%. Calcd for $C_{13}H_9NO_3$: C, 68.72; H, 3.99; N, 6.16%. Treatment with acetic anhydride afforded 1,2-diacetoxy-3-acetyl-4-naphthalenecarbonitrile; white needles from alcohol, mp 159—160 °C. IR: ν_{CN} 2240; $\nu_{C=O}$ 1780, 1700 cm^{-1}. PMR($CDCl_3$), δ: 2.33 (s, 3H, $OCOCH_3$), 2.50 (s, 3H, $OCOCH_3$), 2.78 (s, 3H, $COCH_3$), 7.66—8.00, 8.25—8.39 (m, 4H, aromatic-H). 1,2-Dihydroxy-4-naphthalenecarbonitrile monoacetate [**5**: $R=CH_3$, $R_1=R_3=H$, $R_2=CN$]: white needles (29 mg, 11.6 %), mp 172—174 °C. IR: ν_{OH} 3375; ν_{CN} 2235; $\nu_{C=O}$ 1745 cm^{-1}. PMR($CDCl_3$), δ: 2.46 (s, 3H, CH_3), 7.56—7.87, 8.08—8.50 (m, 5H, aromatic-H+OH). Found: C, 68.86; H, 3.89; N, 6.20%. Calcd for $C_{13}H_9NO_3$: C, 68.72; H, 3.99; N, 6.16%. The acetylate compound was identical with authentic 1,2-diacetoxy-4-naphthalenecarbonitrile (mixed melting point, IR and PMR).

(ii) Propionaldehyde: 1,2-Dihydroxy-3-propionyl-4-naphthalenecarbonitrile [**4**: $R=CH_3CH_2$, $R_1=CN$, $R_2=H$]: orange plates (131 mg, 49.5%), mp 171—174 °C. IR: ν_{OH} 3310; ν_{CN} 2220; $\nu_{C=O}$ 1640 cm^{-1}. PMR ($CDCl_3$), δ: 1.34 (t, 3H, CH_3), 3.57 (q, 2H, CH_2), 6.68 (s, 1H, OH), 7.46—7.60, 8.02—8.28 (m, 4H, aromatic-H), 11.90 (s, 1H, OH). Found: C, 69.64; H, 4.52; N, 5.86%. Calcd for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.60; N, 5.81%. 1,2-Dihydroxy-4-naphthalenecarbonitrile monopropionate [**5**: $R=CH_3CH_2$, $R_1=R_3=H$, $R_2=CN$]: white needles (29 mg, 11%), mp 135—136 °C. IR ν_{OH} 3455; ν_{CN} 2230; $\nu_{C=O}$ 1740 cm^{-1}. PMR ($CDCl_3$), δ: 1.34 (t, 3H, CH_3), 2.75 (q, 2H, CH_2), 7.46—7.68, 8.00—8.30 (m, 6H, aromatic-H+OH). Found: C, 69.53; H, 4.67; N, 5.74%. Calcd for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.60; N, 5.81%.

(iii) Butyraldehyde: 1,2-Dihydroxy-3-butyryl-4-naphthalenecarbonitrile [**4**: $R=CH_3(CH_2)_2$, $R_1=CN$, $R_2=H$]: orange plates (81 mg, 29%), mp 138.5—140 °C. IR: ν_{OH} 3300; ν_{CH} 2965, 2840; ν_{CN} 2230; $\nu_{C=O}$ 1640 cm^{-1}. PMR($CDCl_3$), δ: 1.07 (t, 3H, CH_3), 1.87(sex, 2H, CH_2), 3.50 (t, 2H, $COCH_2$), 6.74 (s, 1H, OH), 7.47—7.68, 8.12—8.34 (m, 4H, aromatic-H), 12.05(s, 1H, OH). Found: C, 70.50; H, 5.21; N, 5.44%. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49%. 1,2-Dihydroxy-4-naphthalenecarbonitrile monobutyrate [**5**: $R=CH_3(CH_3)_2$, $R_1=R_3=H$, $R_2=CN$]: colorless needles (8 mg, 3%), mp 110—111 °C. IR: ν_{OH} 3320; ν_{CN} 2220; $\nu_{C=O}$ 1738 cm^{-1}. PMR($CDCl_3$), δ: 1.07 (t, 3H, CH_3), 1.83 (sex, 2H, CH_2), 2.66 (t, 2H, $COCH_2$), 7.56—7.84, 8.06—8.44 (m, 6H, aromatic-H+OH). Found: C, 70.49; H, 5.06; N, 5.37%. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49%.

(iv) Isobutyraldehyde: 1,2-Dihydroxy-3-isobutyryl-4-naphthalenecarbonitrile [**4**: $R=(CH_3)_2CH$, $R_1=CN$, $R_2=H$]: orange plates (90 mg, 32%), mp 147—149 °C. IR: ν_{OH} 3330; ν_{CH} 2980, 2940; ν_{CN} 2220; $\nu_{C=O}$ 1640 cm^{-1}. PMR($CDCl_3$), δ: 1.34(d, 6H, $(CH_3)_2$), 4.42(sep, 1H, CH), 6.77(s, 1H, OH), 7.50—7.73, 8.15—8.40(m, 4H, aromatic-H), 11.45(s, 1H, OH). Found: C, 70.65; H, 5.10; N, 5.45%. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49%. 1,2-Dihydroxy-4-naphthalenecarbonitrile monoisobutyrate [**5**: $R=(CH_3)_2CH$, $R_1=R_3=H$, $R_2=CN$]: colorless crystals (15 mg, 5.4%), mp 126.5—127 °C. IR: ν_{OH} 3245; ν_{CH} 2990, 2950; ν_{CN} 2235; $\nu_{C=O}$ 1765 cm^{-1}. PMR($CDCl_3$), δ: 1.30 (d, 6H, $(CH_3)_2$), 2.97(sep, 1H, CH), 7.55—7.80, 8.09—8.40(m, 6H, aromatic-H+OH). Found: C, 70.44; H, 5.19; N, 5.53%. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49%.

(v) Valeraldehyde: 1,2-Dihydroxy-3-valeryl-4-naphthalenecarbonitrile [**4**: $R=CH_3(CH_2)_3$, $R_1=CN$, $R_2=H$]: orange plates (91 mg, 31%), mp 112.5—113.0 °C. IR: ν_{OH} 3340; ν_{CH} 2964, 2940, 2880; ν_{CN} 2220; $\nu_{C=O}$ 1638 cm^{-1}. PMR($CDCl_3$), δ: 0.98 (t, 3H, CH_3), 1.30—1.95 (m, 4H, $(CH_2)_2$), 3.50 (t, 2H, $COCH_2$), 6.80 (s, 1H, OH), 7.46—7.65, 8.04—8.20 (m, 4H, aromatic-H), 11.97(s, 1H, OH). Found: C, 71.24; H, 5.69; N, 5.13%. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20%. 1,2-Dihydroxy-4-naphthalenecarbonitrile monovalerate [**5**: $R=CH_3(CH_2)_3$, $R_1=R_3=H$, $R_2=CN$]: white needles (22 mg, 7.4%), mp 118—119 °C. IR: ν_{OH} 3275; ν_{CH} 2960, 2940, 2880; ν_{CN} 2235; $\nu_{C=O}$ 1753 cm^{-1}. PMR(CCl_4), δ: 0.98(t, 3H, CH_3), 1.27—1.90 (m, 4H, $(CH_2)_2$), 2.63 (t, 2H, $COCH_2$), 6.81 (s, 1H, OH), 7.40—8.25 (m, 5H, aromatic-H). Found: C, 71.40; H, 5.55; N, 5.26%. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20%.

(vi) Hexanal: 1,2-Dihydroxy-3-hexanoyl-4-naphthalenecarbonitrile [**4**: $R=CH_3(CH_2)_4$, $R_1=CN$, $R_2=H$]: orange plates (87 mg, 28%), mp 129.5—130.0 °C. IR: ν_{OH} 3300; ν_{CH} 2960, 2940, 2865; ν_{CN} 2220; $\nu_{C=O}$ 1640 cm^{-1}. PMR ($CDCl_3$), δ: 0.92 (t, 3H, CH_3), 1.35—1.88 (m, 6H, $(CH_2)_3$), 3.47 (t, 2H, $COCH_2$), 6.65 (s, 1H, OH), 7.13—8.18 (m, 4H, aromatic-H), 11.83 (s, 1H, OH). Found: C, 71.88; H, 6.10; N, 4.97%. Calcd for $C_{17}H_{17}NO_3$: C, 72.07; H, 6.05; N, 4.94%. 1,2-Dihydroxy-4-naphthalenecarbonitrile monohexanoate [**5**: $R=CH_3(CH_2)_4$, $R_1=R_3=H$, $R_2=CN$]: white needles (15 mg, 5.3%), mp 105.5—106.5 °C. IR: ν_{OH} 3275; ν_{CH} 2960, 2930, 2860; ν_{CN} 2220; $\nu_{C=O}$ 1760 cm^{-1}. PMR(CCl_4), δ: 0.94 (t, 3H, CH_3), 1.31—1.85 (m, 6H, $(CH_2)_3$), 2.61 (t, 2H, $COCH_2$), 6.85 (s, 1H, OH), 7.46—8.25 (m, 5H, aromatic-H). Found: C, 72.33; H, 6.18; N, 4.79%. Calcd for $C_{17}H_{17}NO_3$: C, 72.07; H, 6.05; N, 4.94%.

(vii) Heptanal: 1,2-Dihydroxy-3-heptanoyl-4-naphthalenecarbonitrile [**4**: $R=CH_3(CH_2)_5$, $R_1=CN$, $R_2=H$]: orange plates (94 mg, 28.8%), mp 108—109 °C. IR: ν_{OH} 3300; ν_{CH} 2960, 2930, 2860; ν_{CN} 2220; $\nu_{C=O}$ 1640 cm^{-1}. PMR ($CDCl_3$), δ: 0.90 (t, 3H, CH_3), 1.24—1.94 (m, 8H, $(CH_2)_4$), 3.45 (t, 2H, $COCH_2$), 6.60(s, 1H, OH), 7.17—8.12 (m, 4H, aromatic-H), 11.71(s, 1H, OH). Found: C, 72.65; H, 6.56; N, 4.67%. Calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71%. 1,2-Dihydroxy-4-naphthalenecarbonitrile monoheptanoate [**5**: $R=CH_3(CH_2)_5$, $R_1=R_3=H$, $R_2=CN$]: white needles (15 mg, 4.6%), mp 91—92 °C. IR: ν_{OH} 3290; ν_{CH} 2960, 2935, 2867; ν_{CN} 2235; $\nu_{C=O}$ 1765 cm^{-1}. PMR (CCl_4), δ: 0.90—1.90 (m, 11H, $CH_3(CH_2)_4$), 2.61 (t, 2H, $COCH_2$), 6.82(1H, OH), 7.46—8.25 (m, 5H, aromatic-H). Found: C, 72.29; H, 6.33; N. 4.72%. Calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71%.

(viii) Octanal: 1,2-Dihydroxy-3-octanoyl-4-naphthalenecarbonitrile [**4**: $R=CH_3(CH_2)_6$, $R_1=CN$, $R_2=H$]: orange plates (98 mg, 28.7%), mp 112.0—112.5 °C. IR: ν_{OH} 3315; ν_{CH} 2955, 2940, 2860; ν_{CN} 2215; $\nu_{C=O}$ 1640 cm^{-1}. PMR(CCl_4), δ: 0.86 (t, 3H, CH_3), 1.25—1.90 (m, 10H, $(CH_2)_5$), 3.42 (t, 2H, $COCH_2$), 6.46 (s, 1H, OH), 7.30—

8.10 (m, 4H, aromatic-H), 11.83 (s, 1H, OH). Found: C, 73.04; H, 6.71; N, 4.54%. Calcd for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80, N, 4.54%. 1,2-Dihydroxy-4-naphthalenecarbonitrile monooctanoate [**5**: R=$CH_3(CH_2)_6$, R_1=R_3=H, R_2=CN]: white needles (21 mg, 6.2%), mp 91—92 °C. IR: ν_{OH} 3225; ν_{CH} 2970, 2945, 2870; ν_{CN} 2235; $\nu_{C=O}$ 1760 cm^{-1}. PMR (CCl_4), δ: 0.85 (t, 3H, CH_3), 1.15—1.89 (m, 10 H, $(CH_2)_5$), 2.68 (t, 2H, $COCH_2$), 6.80 (1H, OH), 7.40—8.21 (m, 5H, aromatic-H). Found: C, 73.00; H, 6.57; N, 4.44%. Calcd for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50%.

(ix) Nonanal: 1,2-Dihydroxy-3-nonanoyl-4-naphthalenecarbonitrile [**4**: R=$CH_3(CH_2)_7$, R_1=CN, R_2=H]: orange plates (63 mg, 17.6%), mp 93—94 °C. IR: ν_{OH} 3300; ν_{CH} 2955, 2930, 2860; ν_{CN} 2225; $\nu_{C=O}$ 1638 cm^{-1}. PMR ($CDCl_3$), δ: 0.88 (t, 3H, CH_3), 1.20—1.95 (m, 12H, $(CH_2)_6$), 3.49(t, 2H, $COCH_2$), 6.78 (1H, OH), 7.50—8.30 (m, 4H, aromatic-H), 11.99 (s, 1H, OH). Found: C, 73.49; H, 6.87; N, 4.22%. Calcd for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.12; N, 4.30%. 1,2-Dihydroxy-4-naphthalenecarbonitrile monononanoate [**5**: R=$CH_3(CH_2)_7$, R_1=R_3=H, R_2=CN]: white needles (11 mg, 3.1%), mp 91—92 °C. IR: ν_{OH} 3280; ν_{CH} 2970, 2940, 2865; ν_{CN} 2237; $\nu_{C=O}$ 1765 cm^{-1}. PMR(CCl_4), δ: 0.87 (t, 3H, CH_3), 1.20—1.83 (m, 12H, $(CH_2)_6$), 2.61 (t, 2H, $COCH_2$), 6.91 (1H, OH), 7.45—8.24 (m, 5H, aromatic-H). Found: C, 73.96; H, 7.00; N, 4.21%. Calcd for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.12; N, 4.30%.

(x) Decanal: 1,2-Dihydroxy-3-decanoyl-4-naphthalenecarbonitrile [**4**: R=$CH_3(CH_2)_8$, R_1=CN, R_2=H]: orange plates (82 mg, 22%), mp 156—157 °C. IR: ν_{OH} 3300; ν_{CH} 2925, 2885; ν_{CN} 2215; $\nu_{C=O}$ 1638 cm^{-1}. PMR($CDCl_3$), δ: 0.86—1.86 (m, 17H, $CH_3(CH_2)_7$), 3.52(t, 2H, $COCH_2$), 6.75 (1H, OH), 7.53—8.33 (m, 4H, aromatic-H), 11.98 (s, 1H, OH). Found: C, 74.41; H, 7.26; N, 4.03%. Calcd for $C_{21}H_{25}NO_3$: C, 74.31; H, 7.42; N, 4.13%. 1,2-Dihydroxy-4-naphthalenecarbonitrile monodecanoate [**5**: R=$CH_3(CH_2)_8$, R_1=R_3=H, R_2=CN]: white needles (19 mg, 5.1%), mp 156—157 °C. IR: ν_{OH} 3235; ν_{CH} 2957, 2940, 2858; ν_{CN} 2243; $\nu_{C=O}$ 1760 cm^{-1}. PMR(CCl_4), δ: 0.80—1.96 (br. m, 17H, $CH_3(CH_2)_7$), 2.60 (t, 2H, $COCH_2$), 6.89 (1H, OH), 7.48—8.32 (m, 5H, aromatic-H). Found: C, 74.09; H, 7.50; N, 4.10%. Calcd for $C_{21}H_{25}NO_3$: C, 74.31; H, 7.42; N, 4.13%.

Photo-addition Products of 6-Bromo-1,2-naphthoquinone with Aliphatic Aldehydes. (i) Acetaldehyde: 3-Acetyl-6-bromo-1,2-naphthalenediol [**4**: R=CH_3, R_1=H, R_2=Br]: orange yellow needles (90 mg, 38%), mp 159.5—160.5 °C. IR: ν_{OH} 3440; $\nu_{C=O}$ 1650 cm^{-1}. PMR(CCl_4), δ: 2.78 (s, 3H, CH_3), 5.98 (s, 1H, OH), 7.48—8.05 (m, 4H, aromatic-H), 11.56 (s, 1H, OH). Found: C, 51.17; H, 3.31%. Calcd for $C_{12}H_9BrO_3$: C, 51.27; H, 3.23%. 6-Bromo-1,2-naphthalenediol monoacetate [**5**: R=CH_3, R_1=R_2=H, R_3=Br]: white needles (40 mg, 16.9%), mp 136—137 °C. IR: ν_{OH} 3310; $\nu_{C=O}$ 1742 cm^{-1}. PMR($CDCl_3$), δ: 2.43 (s, CH_3, 70%), 2.52 (s, CH_3, 30%), 7.12—8.18 (m, aromatic-H+OH). Found: C, 51.48; H, 3.17%. Calcd for $C_{12}H_9BrO_3$: C, 51.27; H, 3.23%.

(ii) Propionaldehyde: 3-Propionyl-6-bromo-1,2-naphthalenediol [**4**: R=CH_3CH_2, R_1=H, R_2=Br]: orange prisms (64 mg, 25.7%), mp 143—144.5 °C. IR: ν_{OH} 3375; $\nu_{C=O}$ 1640 cm^{-1}. PMR(CCl_4), δ: 1.30(t, 3H, CH_3), 3.14 (q, 2H, CH_2), 5.92 (s, 1H, OH), 7.37—7.92 (m, 4H, aromatic-H), 11.52 (s, 1H, OH). Found: C, 53.17; H, 3.61%. Calcd for $C_{13}H_{11}BrO_3$: C, 52.91; H, 3.76%. 6-Bromo-1,2-naphthalenediol monopropionate [**5**: R=CH_3CH_2, R_1=R_2=H, R_3=Br]; white crystals (60 mg, 24%), mp 140.5—142 °C. IR: ν_{OH} 3400; $\nu_{C=O}$ 1735 cm^{-1}. PMR($CDCl_3$), δ: 1.31 (t, CH_3, 70%), 1.38 (t, CH_3, 30%), 2.69 (q, CH_2, 70%), 2.78 (q, CH_2, 30%), 7.00—8.00 (m, aromatic-H+OH). Found: C, 52.81; H, 3.65%. Calcd for $C_{13}H_{11}BrO_3$: C, 52.91; H, 3.76%.

(iii) Butyraldehyde: 3-Butyryl-6-bromo-1,2-naphthalenediol [**4**: R=$CH_3(CH_2)_2$, R_1=H, R_2=Br]: orange prisms (67 mg, 25.8%), mp 126.5—128.5 °C. IR: ν_{OH} 3430; ν_{CH} 2960, 2940, 2880; $\nu_{C=O}$ 1655 cm^{-1}. PMR(CCl_4), δ: 1.08 (t, 3H, CH_3), 1.74 (sex, 2H, CH_2), 3.06 (t, 2H, $COCH_2$), 5.95 (s, 1H, OH), 7.38—7.98 (m, 4H, aromatic-H), 11.58 (s, 1H, OH). Found: C, 54.53; H, 4.09%. Calcd for $C_{14}H_{13}BrO_3$: C, 54.39; H, 4.24%. 6-Bromo-1,2-naphthalenediol monobutyrate [**5**: R=$CH_3(CH_2)_2$, R_1=R_2=H, R_3=Br]: white needles (75 mg, 28.8%), mp 131.0—132.5 °C. IR: ν_{OH} 3300; ν_{CH} 2960; $\nu_{C=O}$ 1720 cm^{-1}. PMR($CDCl_3$), δ: 1.08 (t, 3H, CH_3), 1.84 (sex, 2H, CH_2), 2.65 (t, 2H, $COCH_2$), 7.10—8.08 (m, 6H, aromatic-H+OH). Found: C, 54.26; H, 4.37%. Calcd for $C_{14}H_{13}BrO_3$: C, 54.39; H, 4.24%.

(iv) Isobutyraldehyde: 3-Isobutyryl-6-bromo-1,2-naphthalenediol [**4**: R=$(CH_3)_2CH$, R_1=H, R_2=Br]: orange plates (40 mg, 15.4%), mp 116.5—118.0 °C. IR: ν_{OH} 3450; ν_{CH} 2980, 2940; $\nu_{C=O}$ 1650 cm^{-1}. PMR(CCl_4), δ: 1.29 (d, 6H, $(CH_3)_2$), 3.67 (sep, 1H, OH), 5.90 (s, 1H, OH), 7.31—7.96 (m, 4H, aromatic-H), 11.58 (s, 1H, OH). Found: C, 54.72; H, 4.36%. Calcd for $C_{14}H_{13}BrO_3$: C, 54.39; H, 4.24%. 6-Bromo-1,2-naphthalenediol monoisobutyrate [**5**: R=$(CH_3)_2CH$, R_1=R_2=H, R_3=Br]: white prisms (105 mg, 40.4 %), mp 153.0—154.5 °C. IR: ν_{OH} 3440; ν_{CH} 2990, 2950, 2890; $\nu_{C=O}$ 1735 cm^{-1}. PMR($CDCl_3$), δ: 1.40 (d, 6H, $(CH_3)_2$), 2.91 (sep, 1H, CH), 7.02—8.01 (m, 6H, aromatic-H). Found: C, 54.39; H, 4.19%. Calcd for $C_{14}H_{13}BrO_3$: C, 54.39; H, 4.24%.

(v) Valeraldehyde: 3-Valeryl-6-bromo-1,2-naphthalenediol [**4**: R=$CH_3(CH_2)_3$, R_1=H, R_2=Br]: orange needles (49 mg, 18.1%), mp 101—102 °C. IR: ν_{OH} 3450; ν_{CH} 2950, 2880; $\nu_{C=O}$ 1650 cm^{-1}. PMR(CCl_4), δ: 0.98 (t, 3H, CH_3), 1.31—1.88 (m, 4H, $(CH_2)_2$), 3.03 (t, 2H, $COCH_2$), 5.93 (s, 1H, OH), 7.04—7.94 (m, 4H, aromatic-H), 11.65 (s, 1H, OH). Found: C, 55.58; H, 4.52%. Calcd for $C_{15}H_{15}BrO_3$: C, 55.57; H, 4.68%. 6-Bromo-1,2-naphthalenediol monovalerate [**5**: R=$CH_3(CH_2)_3$, R_1=R_2=H, R_3=Br]: white needles (73 mg, 26.9%), mp 121—122 °C. IR: ν_{OH} 3400; ν_{CH} 2960, 2945, 2880; $\nu_{C=O}$ 1722 cm^{-1}. PMR (CCl_4), δ: 0.97 (t, 3H, CH_3), 1.33—1.89 (m, 4H, $(CH_2)_2$), 2.60 (t, 2H, $COCH_2$), 6.10 (s, 1H, OH), 7.00—8.06 (m, 5H, aromatic-H). Found: C, 55.83; H, 4.71%. Calcd for $C_{15}H_{15}BrO_3$: C, 55.75; H, 4.68%.

(vi) Isovaleraldehyde: 3-Isovaleryl-6-bromo-1,2-naphthalenediol [**4**: R=$(CH_3)_2CHCH_2$, R_1=H, R_2=Br]: orange yellow needles (45 mg, 16.6%), mp 117—118 °C. IR: ν_{OH} 3460; ν_{CH} 2960; $\nu_{C=O}$ 1655 cm^{-1}. PMR(CCl_4), δ: 1.04 (d, 6H, $(CH_3)_2$), 2.31 (m, 1H, CH), 2.92 (d, 2H, $COCH_2$), 5.96 (s, 1H, OH), 7.42—7.97 (m, 4H, aromatic-H), 11.69 (s, 1H, OH). Found: C, 55.62; H, 4.61%. Calcd for $C_{15}H_{15}BrO_3$: C, 55.75; H, 4.68%. 6-Bromo-1,2-naphthalenediol monoisovalerate [**5**: R=$(CH_3)_2CHCH_2$, R_1=R_2=H, R_3=Br]: white crystals (75 mg, 27.7%), mp 150—151 °C. IR: ν_{OH} 3420; ν_{CH} 2960; $\nu_{C=O}$ 1720 cm^{-1}. PMR (CCl_4), δ: 1.06 (d, 6H, $(CH_3)_2$), 1.10(d, 6H, $(CH_3)_2$), 2.25(br. m, 2H, CH), 2.45 (t, 2H, $COCH_2$), 2.55 (t, 2H, $COCH_2$), 6.40 (br, 2H, OH), 6.93—8.03 (m, 10H, aromatic-H). Found: C, 55.65; H, 4.75%. Calcd for $C_{15}H_{15}BrO_3$: C, 55.75; H, 4.68.

(vii) Hexanal: 3-Hexanoyl-6-bromo-1,2-naphthalenediol [**4**: R=$CH_3(CH_2)_4$, R_1=H, R_2=Br]: orange plates (64 mg, 22.4%), mp 98—99 °C. IR: ν_{OH} 3450; ν_{CH} 2950, 2875; $\nu_{C=O}$ 1655 cm^{-1}. PMR($CDCl_3$), δ: 0.94 (t, 3H, CH_3), 1.27—1.92 (m, 6H, $(CH_2)_3$), 2.99 (t, 2H, $COCH_2$), 6.02 (s, 1H,

OH), 7.25—7.92 (m, 4H, aromatic-H), 11.65 (s, 1H, OH). Found: C, 56.89; H, 5.14%. Calcd for $C_{16}H_{17}BrO_3$: C, 56.99; H, 5.08%. 6-Bromo-1,2-naphthalenediol monohexanoate [**5**: $R=CH_3(CH_2)_4$, $R_1=R_2=H$, $R_3=Br$]: white crystals (95 mg, 33.6%), mp 106—108 °C. IR: ν_{OH} 3410; ν_{CH} 2970, 2948, 2875; $\nu_{C=O}$ 1725 cm^{-1}. PMR (CCl_4), δ: 0.86—1.90 (m, 11H, $CH_3(CH_2)_4$), 6.19 (br. s, 1H, OH), 7.05—8.05 (m, 5H, aromatic-H). Found: C, 56.71; H, 5.10%. Calcd for $C_{16}H_{17}BrO_3$: C, 56.99; H, 5.08%.

(viii) Heptanal: 3-Heptanoyl-6-bromo-1,2-naphthalenediol [**4**: $R=CH_3(CH_2)_5$, $R_1=H$, $R_2=Br$]: yellow crystals (59 mg, 20%), mp 72—73 °C. IR: ν_{OH} 3440, ν_{CH} 2945, 2875, $\nu_{C=O}$ 1655 cm^{-1}. PMR (CCl_4), δ: 0.91 (t, 3H, CH_3), 1.25—1.90 (m, 8H, $(CH_2)_4$), 3.06 (t, 2H, $COCH_2$), 5.94 (s, 1H, OH), 7.42—7.96 (m, 4H, aromatic-H), 11.67 (s, 1H, OH). Found: C, 58.31; H, 5.52%. Calcd for $C_{17}H_{19}BrO_3$: C, 58.13; H, 5.45%. 6-Bromo-1,2-naphthalenediol monoheptanoate [**5**: $R=CH_3(CH_2)_5$, $R_1=R_2=H$, $R_3=Br$]: white plates (74 mg, 25%), mp 107—108 °C. IR: ν_{OH} 3440; ν_{CH} 2970, 2970, 2945, 2870; $\nu_{C=O}$ 1722 cm^{-1}. PMR(CCl_4), δ: 0.93 (t, 3H, CH_3), 1.26—1.90 (br. m, 8H, $(CH_2)_4$), 2.57 (t, 2H, $COCH_2$), 6.13 (s, 1H, OH), 7.00—8.05 (m, 5H, aromatic-H). Found: C, 58.06; H, 5.50%. Calcd for $C_{17}H_{19}BrO_3$: C, 58.13; H, 5.45%.

(ix) Octanal: 3-Octanoyl-6-bromo-1,2-naphthalenediol [**4**: $R=CH_3(CH_2)_6$, $R_1=H$, $R_2=Br$]: orange plates (71 mg, 23.2%), mp 86—88 °C. IR: ν_{OH} 3440; ν_{CH} 2950, 2925, 2860; $\nu_{C=O}$ 1655 cm^{-1}. PMR(CCl_4), δ: 0.89 (t, 3H, CH_3), 1.20—1.87 (br. m, 10H, $(CH_2)_5$), 3.02 (t, 2H, $COCH_2$), 5.96 (s, 1H, OH), 7.40—7.97 (m, 4H, aromatic-H), 11.67 (s, 1H, OH). Found: C, 59.37; H, 5.63%. Calcd for $C_{18}H_{21}BrO_3$: C, 59.19; H, 5.63%. 6-Bromo-1,2-naphthalenediol monooctanoate [**5**: $R=CH_3(CH_2)_6$, $R_1=R_2=H$, $R_3=Br$]: white crystals (91 mg, 29.7%), mp 99—100 °C. IR: ν_{OH} 3410; ν_{CH} 2960, 2930, 2860; $\nu_{C=O}$ 1738 cm^{-1}. PMR (CCl_4), δ: 0.88 (t, 3H, CH_3), 0.91 (t, 3H, CH_3), 1.81—1.92 (br. m, 20 H, $(CH_2)_{10}$), 2.55 (t, 2H, $COCH_2$), 2.66 (t, 2H, $COCH_2$), 6.14 (2H, OH), 6.88—8.02 (m, 10H, aromatic-H). Found: C, 58.08; H, 5.72%. Calcd for $C_{18}H_{21}BrO_3$: C, 59.19; H, 5.79%.

(x) Nonanal: 3-Nonanoyl-6-bromo-1,2-naphthalenediol [**4**: $R=CH_3(CH_2)_7$, $R_1=H$, $R_2=Br$]: yellow crystals (66 mg, 20.8%), mp 77—78 °C. IR: ν_{OH} 3425; ν_{CH} 2930, 2860; $\nu_{C=O}$ 1655 cm^{-1}. PMR (CCl_4), δ: 0.89 (t, 3H, CH_3), 1.15—1.91 (br. m, 12 H, $(CH_2)_6$), 3.04 (t, 2H, $COCH_2$), 5.94 (s, 1H, OH), 7.41—7.96 (m, 4H, aromatic-H), 11.67 (s, 1H, OH). Found: C, 59.93; H, 6.10%. Calcd for $C_{19}H_{23}BrO_3$: C, 60.17; H, 6.11%. 6-Bromo-1,2-naphthalenediol monononanoate [**5**: $R=CH_3(CH_2)_7$, $R_1=R_2=H$, $R_3=Br$]: white crystals (98 mg, 30.3%), mp 97—98 °C. IR: ν_{OH} 3430; ν_{CH} 2940, 2860; $\nu_{C=O}$ 1740 cm^{-1}. PMR (CCl_4), δ: 0.85—1.92 (br. m, 30H, $CH_3(CH_2)_6$), 2.56 (t, 2H, $COCH_2$), 2.68 (t, 2H, $COCH_2$), 6.07 (1H, OH), 6.19 (1H, OH), 6.91—8.03 (m, 10 H, aromatic-H). Found: C, 60.24; H, 6.27%. Calcd for $C_{19}H_{23}BrO_3$: C, 60.17; H, 6.11%.

(xi) Decanal: 3-Decanoyl-6-bromo-1,2-naphthalenediol [**4**: $R=CH_3(CH_2)_8$, $R_1=H$, $R_2=Br$]: orange crystals (38 mg, 11.5%), mp 92—93 °C. IR: ν_{OH} 3420; ν_{CH} 2910, 2870; $\nu_{C=O}$ 1650 cm^{-1}. PMR(CCl_4), δ: 0.86 (t, 3H, CH_3), 1.16—1.88 (br. m, 14H, $(CH_2)_7$), 3.02 (t, 2H, $COCH_2$), 5.91 (s, 1H, OH), 7.41—7.94 (m, 4H, aromatic-H), 11.65 (s, 1H, OH). Found: C, 61.08; H, 6.33%. Calcd for $C_{20}H_{25}BrO_3$: C, 61.08; H, 6.41%. 6-Bromo-1,2-naphthalenediol monodecanoate [**5**: $R=CH_3(CH_2)_8$, $R_1=R_2=H$, $R_3=Br$]: white crystals (121 mg, 36.7%), mp 89.0—89.5 °C. IR: ν_{OH} 3425; ν_{CH} 2940, 2860; $\nu_{C=O}$ 1720 cm^{-1}. PMR (CCl_4), δ: 0.88 (t, 3H, CH_3), 1.20—1.87 (br. m. 14H, $(CH_2)_7$), 2.56 (t, 2H, $COCH_2$), 6.14 (1H, OH), 7.02—8.06 (m, 5H, aromatic-H). Found: C, 61.24; H, 6.50%. Calcd for $C_{20}H_{25}BrO_3$: C, 61.08; H, 6.41%.

Photo-addition Products of 6-Methyl-1,2-naphthoquinone with Aliphatic Aldehydes. (i) Acetaldehyde: 3-Acetyl-6-methyl-1,2-naphthalenediol [**4**: $R=CH_3$, $R_1=H$, $R_2=CH_3$]: orange plates (25 mg, 10%), mp 156—157 °C. IR: ν_{OH} 3330 (br); $\nu_{C=O}$ 1650 cm^{-1}. PMR(CCl_4), δ: 2.26 (s, 3H, CH_3), 2.69 (s, 3H, CH_3), 5.86 (s, 1H, OH), 7.24—8.04 (m, 4H, aromatic-H), 11.47 (s, 1H, OH). Found: C, 72.21; H, 5.63%. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59%. 6-Methyl-1,2-naphthalenediol monoacetate [**5**: $R=CH_3$, $R_1=R_2=H$, $R_3=CH_3$]: white plates (15 mg, 6%), mp 127—128 °C. IR: ν_{OH} 3360; $\nu_{C=O}$ 1720 cm^{-1}. PMR(CCl_4), δ: 2.29 (s, 3H, $COCH_3$), 2.39 (s, 3H, $COCH_3$), 2.47 (s, 6H, CH_3), 6.10 (2H, OH), 7.08—8.10 (m, 10H, aromatic-H). Found: C, 72.10; H, 5.48%. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59%.

(ii) Propionaldehyde: 3-Propionyl-6-methyl-1,2-naphthalenediol [**4**: $R=CH_3CH_2$, $R_1=H$, $R_2=CH_3$]; yellow plates (55 mg, 15.2%), mp 148—149 °C. IR: ν_{OH} 3448; $\nu_{C=O}$ 1647 cm^{-1}. PMR(CCl_4), δ: 1.27 (t, 3H, CH_3), 2.45 (s, 3H, CH_3), 3.14 (q, 2H, CH_2), 5.85 (s, 1H, OH), 7.16—7.95 (m, 4H, aromatic-H), 11.03 (s, 1H, OH). Found: C, 73.22; H, 5.59%. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13%. 6-Methyl-1,2-naphthalenediol monopropionate [**5**: $R=CH_3CH_2$, $R_1=R_2=H$, $R_3=CH_3$]: white crystals (50 mg, 13.9%), mp 114—116 °C. IR: ν_{OH} 3400 (br); $\nu_{C=O}$ 1722 cm^{-1}. PMR(CCl_4), δ: 1.33 (t, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.72 (q, 2H, CH_2), 5.81 (1H, OH), 6.93—7.53 (m, 5H, aromatic-H). Found: C, 72.89; H, 6.05%. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13%.

(iii) Butyraldehyde: 3-Butyryl-6-methyl-1,2-naphthalenediol [**4**: $R=CH_3(CH_2)_2$, $R_1=H$, $R_2=CH_3$]: yellow orange needles (25 mg, 10.4%), mp 117—118 °C. IR: ν_{OH} 3490; ν_{CH} 2960, 2940, 2880; $\nu_{C=O}$ 1635 cm^{-1}. PMR (CCl_4), δ: 1.05 (t, 3H, CH_3), 1.80 (sex, 2H, CH_2), 2.43 (s, 3H, CH_3), 3.04 (t, 2H, $COCH_2$), 5.87 (s, 1H, OH), 7.18—7.96 (m, 4H, aromatic-H), 11.55 (s, 1H, OH). Found: C, 74.00; H, 6.68%. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60%. 6-Methyl-1,2-naphthalenediol monobutyrate [**5**: $R=CH_3(CH_2)_2$, $R_1=R_2=H$, $R_3=CH_3$]: white plates (28 mg, 11.5%), mp 99.0—99.5 °C. IR: ν_{OH} 3300(br); ν_{CH} 2980, 2945, 2890; $\nu_{C=O}$ 1725 cm^{-1}. PMR (CCl_4), δ: 1.03 (t, 3H, CH_3), 1.08 (t, 3H, CH_3), 1.65—1.96 (m, 4H, CH_2), 2.45 (s, 3H, CH_3), 2.54 (t, 2H, $COCH_2$), 2.66 (t, 2H, $COCH_2$), 6.00 (2H, OH), 6.91—8.07 (m, 10H, aromatic-H). Found: C, 73.71; H, 6.51%. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60%.

(iv) Isobutyraldehyde: 3-Isobutyryl-6-methyl-1,2-naphthalenediol [**4**: $R=(CH_3)_2CH$, $R_1=H$, $R_2=CH_3$]: yellow prisms (31 mg, 7.8%), mp 155—156 °C. IR: ν_{OH} 3450; ν_{CH} 2990, 2940; $\nu_{C=O}$ 1645 cm^{-1}. PMR(CCl_4), δ: 1.29 (d, 6H, $(CH_3)_2$), 2.42(s, 3H, CH_3), 3.75 (sep. 1H, OH), 5.90 (s, 1H, OH), 7.20—8.00 (m, 4H, aromatic-H), 11.65 (s, 1H, OH). Found: C, 73.63; H, 6.47%. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60%. 6-Methyl-1,2-naphthalenediol monoisobutyrate [**5**: $R=(CH_3)_2CH$, $R_1=R_2=H$, $R_3=CH_3$]: white needles (126 mg, 31.9%), mp 118—119 °C. IR: ν_{OH} 3325; ν_{CH} 2980, 2930, 2890; $\nu_{C=O}$ 1720 cm^{-1}. PMR(CCl_4), δ: 1.34 (d, 6H, $(CH_3)_2$), 2.46 (s, 3H, CH_3), 2.82 (sep, 1H, CH), 5.96 (1H, OH), 6.94—8.08 (m, 5H, aromatic-H). Found: C, 73.49; H, 6.65%. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60%.

(v) Valeraldehyde: 3-Valeryl-6-methyl-1,2-naphthalenediol [**4**: $R=CH_3(CH_2)_3$, $R_1=H$, $R_2=CH_3$]: yellowish orange needles (58 mg, 13.5%), mp 101—102 °C. IR: ν_{OH} 3410; ν_{CH} 2960, 2930, 2880; $\nu_{C=O}$ 1650 cm^{-1}. PMR(CCl_4), δ: 1.01 (t, 3H, CH_3), 1.30—1.90 (m, 4H, $(CH_2)_2$), 2.48 (s, 3H, CH_3), 3.10 (t, 2H, $COCH_2$), 5.88 (s, 1H, OH), 7.10—8.01 (m, 4H,

aromatic-H), 11.61 (s, 1H, OH). Found: C, 74.43; H, 7.08%. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02%. 6-Methyl-1,2-naphthalenediol monovalerate [**5**: $R=CH_3(CH_2)_3$, $R_1=R_2=H$, $R_3=CH_3$]: white needles (66 mg, 15.4%), mp 92—94 °C. IR: ν_{OH} 3390; ν_{CH} 2960, 2930, 2880; $\nu_{C=O}$ 1722 cm^{-1}. PMR(CCl_4), δ: 0.96 (t, 3H, CH_3), 1.30—1.86 (m, 4H, $(CH_2)_2$), 2.46 (s, 3H, CH_3), 2.55 (t, 2H, $COCH_2$), 5.98 (s, 1H, OH), 6.29—8.07 (m, 5H, aromatic-H). Found: C, 74.28; H, 6.95%. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02%.

(vi) Isovaleraldehyde: 3-Isovaleryl-6-methyl-1,2-naphthalenediol [**4**: $R=(CH_3)_2CHCH_2$, $R_1=H$, $R_2=CH_3$]: yellow needles (41 mg, 10%), mp 89—91 °C. IR: ν_{OH} 3400; ν_{CH} 2970, 2890; $\nu_{C=O}$ 1645 cm^{-1}. PMR(CCl_4), δ: 1.05 (d, 6H, $(CH_3)_2$), 2.05 (m, 1H, CH), 2.45 (s, 3H, CH_3), 2.94 (d, 2H, $COCH_2$), 5.87 (s, 1H, OH), 7.25—7.94 (4H, aromatic-H), 11.60 (s, 1H, OH). Found: C, 74.33; H, 6.89%. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02%. 6-Methyl-1,2-naphthalenediol monoisovalerate [**5**: $R=(CH_3)_2CHCH_2$, $R_1=R_2=H$, $R_3=CH_3$]: white needles (89 mg, 21%), mp 99—100 °C. IR: ν_{OH} 3410 (br); ν_{CH} 2980; $\nu_{C=O}$ 1735 cm^{-1}. PMR(CCl_4), δ: 1.06 (d, 6H, $(CH_3)_2$), 1.10 (d, 6H, $(CH_3)_2$), 2.26 (br. m, 2H, CH), 2.44 (d, 2H, $COCH_2$), 2.46 (s, 6H, CH_3), 2.56 (d, 2H, $COCH_2$), 5.74 (1H, OH), 5.94 (1H, OH), 6.92—8.08 (m, 10H, aromatic-H). Found: C, 74.21; H, 7.01%. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02%.

(vii) Hexanal: 3-Hexanoyl-6-methyl-1,2-naphthalenediol [**4**: $R=CH_3(CH_2)_4$, $R_1=H$, $R_2=CH_3$]: yellowish orange needles (81 mg, 17.4%), mp 88—89 °C. IR: ν_{OH} 3430; ν_{CH} 2960, 2940, 2880; $\nu_{C=O}$ 1643 cm^{-1}. PMR(CCl_4), δ: 0.80—1.90 (br. m, 9H, $CH_3(CH_2)_3$), 2.43 (s, 3H, CH_3), 3.04 (t, 2H, $COCH_2$), 5.85 (s, 1H, OH), 7.20—8.00 (4H, aromatic-H), 11.58 (s, 1H, OH). Found: C, 74.73; H, 7.52%. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40%. 6-Methyl-1,2-naphthalenediol monohexanoate [**5**: $R=CH_3(CH_2)_4$, $R_1=R_2=H$, $R_3=CH_3$]: white lieves (48 mg, 11%), mp 78—80 °C. IR: ν_{OH} 3390; ν_{CH} 2970, 2930, 2870; $\nu_{C=O}$ 1720 cm^{-1}. PMR (CCl_4), δ: 0.80—2.00 (br. m, 18H, $CH_3(CH_2)_3$), 2.48 (s, 6H, CH_3), 2.54 (t, 2H, $COCH_2$), 2.68 (t, 2H, $COCH_2$), 6.00 (2H, OH), 6.92—8.15 (m, 10H, aromatic-H). Found C, 75.11; H, 7.48%. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40%.

(viii) Heptanal: 3-Heptanoyl-6-methyl-1,2-naphthalenediol [**4**: $R=CH_3(CH_2)_5$, $R_1=H$, $R_2=CH_3$]: orange needles (62 mg, 14%), mp 76—77 °C. IR: ν_{OH} 3370; ν_{CH} 2960, 2930, 2860; $\nu_{C=O}$ 1640 cm^{-1}. PMR(CCl_4), δ: 0.90 (t, 3H, CH_3), 1.23—1.86 (br. m, 8H, $(CH_2)_4$), 2.42 (s, 3H, CH_3), 3.03 (t, 2H, $COCH_2$), 5.85 (s, 1H, OH), 7.18—7.95 (4H, aromatic-H), 11.54 (s, 1H, OH). Found: C, 75.54; H, 7.60%. Calcd for $C_{18}H_{22}O_3$: C, 75.50; H, 7.74%. 6-Methyl-1,2-naphthalenediol monoheptanoate [**5**: $R=CH_3(CH_2)_5$, $R_1=R_2=H$, $R_3=CH_3$]: white plates (41 mg, 9.2%), mp 76—77 °C. IR: ν_{OH} 3375 (br); ν_{CH} 2960, 2930, 2860; $\nu_{C=O}$ 1735, 1710 cm^{-1}. PMR(CCl_4), δ: 0.90 (t, 3H, CH_3), 1.25—1.88 (br. m, 8H, $(CH_2)_4$), 2.45 (s, 3H, CH_3), 2.56 (t, 2H, $COCH_2$), 5.95 (s, 1H, OH), 6.95—8.10 (m, 5H, aromatic-H). Found: C, 75.26; H, 7.81%. Calcd for $C_{18}H_{22}O_3$: C, 75.50; H, 7.74%.

(ix) Octanal: 3-Octanoyl-6-methyl-1,2-naphthalenediol [**4**: $R=CH_3(CH_2)_6$, $R_1=H$, $R_2=CH_3$]: orange plates (21 mg, 4.4%), mp 76—77 °C. IR: ν_{OH} 3440; ν_{CH} 2925, 2860; $\nu_{C=O}$ 1655 cm^{-1}. PMR(CCl_4), δ: 0.90 (t, 3H, CH_3), 1.25—1.88 (br. m, 10H, $(CH_2)_5$), 2.43 (s, 6H, CH_3), 3.05 (t, 2H, $COCH_2$), 5.84 (s, 1H, OH), 7.20—7.97 (4H, aromatic-H), 11.57 (s, 1H, OH). Found: C, 75.63; H, 7.92%. Calcd for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05%. 6-Methyl-1,2-naphthalenediol monooctanoate [**5**: $R=CH_3(CH_2)_6$, $R_1=R_2=H$, $R_3=CH_3$]: white crystals (22 mg, 4.7%), mp 77—78 °C. IR: ν_{OH} 3425; ν_{CH} 2960, 2930, 2860; $\nu_{C=O}$ 1740 cm^{-1}. PMR(CCl_4), δ: 0.88—1.88 (br. m, 26H, $CH_3(CH_2)_5$), 2.43 (s, 6H, CH_3), 2.53 (t, 2H, $COCH_2$), 2.66 (t, 2H, $COCH_2$), 5.74 (1H, OH), 6.00 (1H, OH), 6.93—8.07 (m, 10H, aromatic-H). Found: C, 75.89; H, 7.86%. Calcd for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05%.

(x) Nonanal: 3-Nonanoyl-6-methyl-1,2-naphthalenediol [**4**: $R=CH_3(CH_2)_7$, $R_1=H$, $R_2=CH_3$]: reddish orange plates (72 mg, 13.8%), mp 74—75 °C. IR: ν_{OH} 3470; ν_{CH} 2940, 2865; $\nu_{C=O}$ 1650 cm^{-1}. PMR(CCl_4), δ: 0.87 (t, 3H, CH_3), 1.18—1.88 (br. m, 12H, $(CH_2)_6$), 2.42 (s, 3H, CH_3), 3.00 (t, 2H, $COCH_2$), 5.86 (s, 1H, OH), 7.16—7.95 (4H, aromatic-H), 11.54 (s, 1H, OH). Found: C, 76.40; H, 8.39%. Calcd for $C_{20}H_{26}O_3$): C, 76.40; H, 8.33%. 6-Methyl-1,2-naphthalenediol mononononanoate [**5**: $R=CH_3$, $R_1=R_2=H$, $R_3=CH_3$]: white crystals (105 mg, 20.2%), mp 76—77 °C. IR: ν_{OH} 3440; ν_{CH} 2940, 2870; $\nu_{C=O}$ 1740 cm^{-1}. PMR(CCl_4), δ: 0.80—1.88 (br. m, 34H, $CH_3(CH_2)_7$), 2.43 (s, 6H, CH_3), 2.53 (t, 2H, $COCH_2$), 2.64 (t, 2H, $COCH_2$), 5.85 (1H, OH), 6.05 (1H, OH), 6.93—8.07 (m, 10H, aromatic-H). Found: C, 76.09; H, 8.39%. Calcd for $C_{20}H_{26}O_3$: C, 76.40; H, 8.33%.

(xi) Decanal: 3-Decanoyl-6-methyl-1,2-naphthalenediol [**4**: $R=CH_3(CH_2)_8$, $R_1=H$, $R_2=CH_3$]: orange plates (53 mg, 9.8%), mp 70—71 °C. IR: ν_{OH} 3450; ν_{CH} 2930, 2855; $\nu_{C=O}$ 1650 cm^{-1}. PMR(CCl_4), δ: 0.87 (t, 3H, CH_3), 1.18—1.90 (br. m, 14H, $(CH_2)_7$), 2.41 (s, 3H, CH_3), 3.02 (t, 2H, $COCH_2$), 5.85 (s, 1H, OH), 7.18—7.95 (4H, aromatic-H), 11.55 (s, 1H, OH). Found: C, 76.75; H, 8.43%. Calcd for $C_{21}H_{28}O_3$: C, 76.79; H, 8.59%. 6-Methyl-1,2-naphthalenediol monodecanoate [**5**: $R=CH_3(CH_2)_8$, $R_1=R_2=H$, $R_3=CH_3$]: white crystals (41 mg, 7.6%), mp 64—65 °C. IR: ν_{OH} 3420; ν_{CH} 2930, 2860; $\nu_{C=O}$ 1740, 1720 cm^{-1}. PMR(CCl_4), δ: 0.81—1.92 (br. m, 34 H, $CH_3(CH_2)_7$), 2.44 (s, 6H, CH_3), 2.55 (t, 2H, $COCH_2$), 2.67 (t, 2H, $COCH_2$), 5.82 (1H, OH), 6.03 (1H, OH), 6.93—8.07 (m,10H, aromatic-H). Found: C, 77.03, H, 8.49%. Calcd for $C_{21}H_{28}O_3$: C, 76.79; H, 8.59%.

Irradiation of 3-Chloro-1,2-naphthoquinone in the Presence of Acetaldehyde. *(a)* A benzene solution of quinone (200 mg, 1.04 mmol) and acetaldehyde (500 mg) was irradiated for 4 days. Paraldehyde was detected by PMR analysis of the reaction mixture. The solvent and paraldehyde were removed at 60 °C under reduced pressure, and the residue was worked up as usual.

(b) The quinone (300 mg) in acetaldehyde (15 g) was irradiated for 5 days; the metaldehyde which deposited (120 mg) was filtered off and the paraldehyde (13.5 g) was removed at 60 °C under reduced pressure, then the residue was chromatographed over silica gel.

Photo-addition Products of 3-Chloro-1,2-naphthoquinone with Aliphatic Aldehydes. *(i) Acetaldehyde*: 3-Chloro-1,2-naphthalenediol monoacetate [**5**: $R=CH_3$, $R_1=Cl$, $R_2=R_3=H$] white needles (95 mg, 38.7%), mp 149—150 °C. IR: ν_{OH} 3335 (br), $\nu_{C=O}$ 1757 cm^{-1}. PMR ($CDCl_3$), δ: 2.48 (s, 3H, CH_3), 7.33—8.24(m, 6H, aromatic-H+OH). Found: C, 60.85; H, 3.88%. Calcd for $C_{12}H_9ClO_3$: C, 60.90; H, 3.83%. 3-Chloro-4-acetyl-1,2-naphthoquinone: reddish orange needles (12 mg, 4.9%), mp 197—200 °C. IR: $\nu_{C=O}$ 1700, 1685 cm^{-1}. MS, *m/e*: 234 (M^+), 206 (M−CO), 199 (M−Cl), 178 (M−2CO), 171 (M−Cl−CO). PMR($CDCl_3$), δ: 2.30 (s, 3H, CH_3), 7.04—8.16 (m, 4H, aromatic-H). 3-Acetyl-1,2-naphthalenediol(2.1 mg, 1%) was identical (IR spectrum) with the photo-adduct of 1,2-naphthoquinone and acetaldehyde.

(ii) Propionaldehyde: 3-Chloro-1,2-naphthalenediol mono-

propionate [**5**: R=CH_3CH_2, R_1=Cl, R_2=R_3=H]: white needles (75 mg, 28.9 %), mp 107—108 °C. IR: ν_{OH} 3300; $\nu_{C=O}$ 1740 cm^{-1}. PMR($CDCl_3$), δ: 1.36 (t, 3H, CH_3), 2.77 (q, 2H, CH_2), 7.33—8.22 (m, 6H, aromatic-H). Found: C, 62.37; H, 4.46%. Calcd for $C_{13}H_{11}ClO_3$: C, 62.29; H, 4.42%. 3-Propionyl-1,2-naphthalenediol (8 mg, 3.6%) was identical (IR spectrum) with the photo-adduct of 1,2-naphthoquinone and propionaldehyde.

(iii) Butyraldehyde: 3-Chloro-1,2-naphthalenediol monobutyrate [**5**: R=$CH_3(CH_2)_2$, R_1=Cl R_2=R_3=H): white needles (70 mg, 24.4%), mp 116.5—118 °C. IR: ν_{OH} 3360; ν_{CH} 2960, 2930, 2880; $\nu_{C=O}$ 1735 cm^{-1}. PMR ($CDCl_3$), δ: 1.10 (t, 3H, CH_3), 1.14 (t, 3H, CH_3), 1.88 (sex, 2H, CH_2), 1.92 (sex, 2H, CH_2), 2.75 (t, 2H, $COCH_2$), 2.79 (t, 2H, $COCH_2$), 7.29—8.15 (m, 12H, aromatic-H). Found: C, 63.54; H, 4.88%. Calcd for $C_{14}H_{13}ClO_3$: C, 63.52; H, 4.95%. 3-Butyryl-1,2-naphthalenediol (11.5 mg, 4.6%) was identical (IR and PMR spectra) with the photo-adduct of 1,2-naphthoquinone and butyraldehyde.

(iv) Isobutyraldehyde: 3-Chloro-1,2-naphthalenediol monoisobutyrate [**5**: R=$(CH_3)_2CH$, R_1=Cl, R_2=R_3=H]: white needles (92 mg, 33.5%), mp 116.0—117.5 °C. IR: ν_{OH} 3405; ν_{CH} 2990, 2940; $\nu_{C=O}$ 1735 cm^{-1}. PMR ($CDCl_3$), δ: 1.42 (d, 6H, $(CH_3)_2$), 1.46 (d, 6H, $(CH_3)_2$), 3.02 (sep, 1H, CH), 3.06 (sep, 1H, CH), 5.72 (1H, OH), 5.84 (1H, OH), 7.01—8.23 (m, 10H, aromatic-H). Found: C, 63.33; H, 4.99%. Calcd for $C_{14}H_{13}ClO_3$: C, 63.52; H, 4.95%. 3-Isobutyryl-1,2-naphthalenediol (15 mg, 5.9%) was identical (IR and PMR spectra) with the photo-adduct of 1,2-naphthoquinone and isobutyraldehyde.

(v) Valeraldehyde: 3-Chloro-1,2-naphthalenediol monovalerate [**5**: R=$CH_3(CH_2)_3$, R_1=Cl, R_2=R_3=H]: white needles (80 mg, 27.7%), mp 89—90 °C. IR: ν_{OH} 3275; ν_{CH} 2960, 2940; $\nu_{C=O}$ 1735 cm^{-1}. PMR (CCl_4), δ: 0.92 (t, 3H, CH_3), 1.30—1.88 (m, 4H, $(CH_2)_2$), 2.60 (t, 2H, $COCH_2$), 6.10 (1H, OH), 7.30—8.12 (m, 5H, aromatic-H). Found: C, 64.57; H, 5.46%. Calcd for $C_{15}H_{15}ClO_3$: C, 64.64; H, 5.42%. 3-Chloro-4-valeryl-1,2-naphthoquinone: orange plates (9 mg, 3.1%), mp 144.5—145.5 °C. IR: ν_{OH} 2969, 2940, 2883; $\nu_{C=O}$ 1704, 1688 cm^{-1}. PMR(CCl_4), δ: 0.97 (t, 3H, CH_3), 1.33—1.82 (m, 4H, $(CH_2)_2$), 6.91—8.08 (m, 4H, aromatic-H). MS, *m/e*: 276 (M^+), 241 (M−Cl), 213 (M−CO−Cl), 191 (M−COR). Found: C, 65.02; H, 4.81%. Calcd for $C_{15}H_{13}ClO_3$: C, 65.11; H, 4.74%. 3-Valeryl-1,2-naphthalenediol (15 mg, 5.9%) was identical (IR and PMR spectra) with the photo-adduct of 1,2-naphthoquinone and valeraldehyde.

(vi) Isovaleraldehyde: 3-Chloro-1,2-naphthalenediol monoisovalerate [**5**: R=$(CH_3)_2CHCH_2$, R_1=Cl, R_2=R_3=H]: white needles (93 mg, 32.2%), mp 125—125.5 °C. IR: ν_{OH} 3315, ν_{CH} 2972, 2922, 2880; $\nu_{C=O}$ 1735 cm^{-1}. PMR($CDCl_3$), δ: 1.08 (d, 6H, $(CH_3)_2$), 2.30 (m, 1H, CH), 2.60 (d, 2H, $COCH_2$), 7.40—8.20 (m, 6H, aromatic-H+OH). Found: C, 64.66; H, 5.38%. Calcd for $C_{15}H_{15}ClO_3$: C, 64.66; H, 5.42%. 3-Chloro-4-isovaleryl-1,2-naphthoquinone: reddish orange plates (12 mg, 4.2 %), mp 138—140 °C. IR: ν_{CH} 2970, 2942, 2885; $\nu_{C=O}$ 1704, 1687 cm^{-1}. PMR(CCl_4), δ: 1.07 (d, 6H, $(CH_3)_2$), 2.35 (m, 1H, CH), 2.70 (d, 2H, $COCH_2$), 6.94—8.10 (m, 4H, aromatic-H). Found: C, 65.00; H, 4.61%. Calcd for $C_{15}H_{13}ClO_3$: C, 65.11; H, 4.74%. 3-Isovaleryl-1,2-naphthalenediol(3.8 mg, 1.5%) was identical (PMR spectrum) with the photo-adduct of 1,2-naphthoquinone and isovaleraldehyde.

(vii) Hexanal: 3-Chloro-1,2-naphthalenediol monohexanoate [**5**: R=$CH_3(CH_2)_4$, R_1=Cl, R_2=R_3=H]: white needles (89 mg, 29.3%), mp 95.5—96.5 °C. IR: ν_{OH} 3200; ν_{CH} 2960, 2940; $\nu_{C=O}$ 1735 cm^{-1}. PMR($CDCl_3$), δ: 0.92 (t, 3H, CH_3), 1.30—1.90 (m, 6H, $(CH_2)_3$), 2.69 (t, 2H, $COCH_2$), 7.40—8.20 (m, 6H, aromatic-H+OH). Found: C, 65.73; H, 5.83%. Calcd for $C_{16}H_{17}ClO_3$: C, 65.64; H, 5.85%. 3-Chloro-4-hexanoyl-1,2-naphthoquinone: orange plates, mp 111—112 °C. IR: ν_{CH} 2960, 2935, 2870; $\nu_{C=O}$ 1705, 1680 cm^{-1}. 3-Hexanoyl-1,2-naphthalenediol was identical (IR spectrum) with the photo-adduct of 1,2-naphthoquinone and hexanal.

(viii) Heptanal: 3-Chloro-1,2-naphthalenediol monoheptanoate [**5**: R=$CH_3(CH_2)_5$, R_1=Cl, R_2=R_3=H]: white needles (103 mg, 32.4%), mp 80.5—82.0 °C. IR: ν_{OH} 3422; ν_{CH} 2958, 2935, 2870; $\nu_{C=O}$ 1735 cm^{-1}. PMR($CDCl_3$), δ: 0.92 (t, 3H, CH_3), 1.20—1.90 (m, 8H, $(CH_2)_4$), 2.70 (t, 2H, $COCH_2$), 5.80 (1H, OH), 7.40—8.20 (m, 5H, aromatic-H). Found: C, 66.71; H, 6.20%. Calcd for $C_{17}H_{19}ClO_3$: C, 66.56; H, 6.24%. 3-Chloro-4-heptanoyl-1,2-naphthoquinone: yellow crystals (12 mg, 3.8%), mp 105—106 °C. IR: ν_{CH} 2967, 2940, 2874; $\nu_{C=O}$ 1708, 1685 cm^{-1}. PMR (CCl_4), δ: 0.90 (t, 3H, CH_3), 1.23—1.84 (m, 8H, $(CH_2)_4$), 2.77 (t, 2H, $COCH_2$), 6.95—8.14 (m, 4H, aromatic-H). Found: C, 66.89; H, 5.57%. Calcd for $C_{17}H_{17}ClO_3$: C, 67.00; H, 5.62%. 3-Heptanoyl-1,2-naphthalenediol (23 mg, 8.2%) was identical (IR and PMR spectra) with the photo-adduct of 1,2-naphthoquinone and heptanal.

(ix) Octanal: 3-Chloro-1,2-naphthalenediol monooctanoate [**5**: R=$CH_3(CH_2)_6$, R_1=Cl, R_2=R_3=H]: white needles (47 mg, 14.1%), mp 79.5—80.5 °C. IR: ν_{OH} 3290, ν_{CH} 2960, 2935, 2860; $\nu_{C=O}$ 1737 cm^{-1}. PMR($CDCl_3$), δ: 0.88—1.90 (br. m, 13H, $CH_3(CH_2)_5$), 2.72 (t, 2H, $COCH_2$), 5.80 (1H, OH), 7.40—8.20 (m, 5H, aromatic-H). Found: C, 67.50; H, 6.30%. Calcd for $C_{18}H_{21}ClO_3$: C, 67.39; H, 6.60%. 3-Octanoyl-1,2-naphthalenediol (15 mg, 5.1%) was identical (IR and PMR spectra) with the photo-adduct of 1,2-naphthoquinone and octanal.

(x) Nonanal: 3-Chloro-1,2-naphthalenediol mononononanoate [**5**: R=$CH_3(CH_2)_7$, R_1=Cl, R_2=R_3=H]: white needles (72 mg, 20.7%), mp 76—77 °C. IR: ν_{OH} 3280; ν_{CH} 2970, 2945, 2870; $\nu_{C=O}$ 1735 cm^{-1}. PMR($CDCl_3$), δ: 0.88—1.90 (br. m, 15H, $CH_3(CH_2)_6$), 2.72 (t, 2H, $COCH_2$), 7.40—8.20 (m, 6H, aromatic-H+OH). Found: C, 68.15; H, 6.83%. Calcd for $C_{19}H_{23}ClO_3$: C, 68.15; H, 6.92%. 3-Chloro-4-nonanoyl-1,2-naphthoquinone: orange crystals (18 mg, 5.2%), mp 108—109 °C. IR: ν_{CH} 2967, 2938, 2870; $\nu_{C=O}$ 1720, 1680 cm^{-1}. PMR(CCl_4), δ: 0.88 (t, 3H, CH_3), 1.17—1.86 (br. m, 12H, $(CH_2)_6$), 2.78 (t, 2H, $COCH_2$), 6.92—8.07 (m, 4H, aromatic-H). Found: C, 68.64; H, 6.31%. Calcd for $C_{19}H_{21}ClO_3$: C, 68.57; H, 6.36%. 3-Nonanoyl-1,2-naphthalenediol (27 mg, 9.4%) was identical (IR and PMR spectra) with the photo-adduct of 1,2-naphthoquinone and nonanal.

(xi) Decanal: 3-Chloro-1,2-naphthalenediol monodecanoate [**5**: R=$CH_3(CH_2)_8$, R_1=Cl, R_2=R_3=H]: white needles (79 mg, 21.8%), mp 67—68 °C. IR: ν_{OH} 3290; ν_{CH} 2960, 2930, 2860; $\nu_{C=O}$ 1735 cm^{-1}. PMR($CDCl_3$), δ: 0.84 (t, 3H, CH_3), 1.10—1.90 (br. m, 14H, $(CH_2)_7$), 2.68 (t, 2H, $COCH_2$), 7.40—8.20 (m, 6H, aromatic-H+OH). Found: C, 69.10; H, 7.37%. Calcd for $C_{20}H_{25}ClO_4$: C, 68.86; H, 7.22%. 3-Chloro-4-decanoyl-1,2-naphthoquinone: orange plates (19 mg, 5.3%), mp 103—104 °C. IR: ν_{CH} 2986, 2935, 2865; $\nu_{C=O}$ 1718, 1678 cm^{-1}. PMR ($CDCl_3$), δ: 0.87 (t, 3H, CH_3), 1.17—1.85 (br. m, 14H, $(CH_2)_7$), 2.85 (t, 2H, $COCH_2$), 6.98—8.14 (m, 4H, aromatic-H). MS; *m/e* 346 (M^+), 311 (M−Cl), 283 (M−CO−Cl). Found: C, 69.33; H, 6.54%. Calcd for $C_{20}H_{23}ClO_3$: C, 69.26; H, 6.68%. 3-Decanoyl-1,2-naphthalenediol (18 mg, 5.5%) was identical (IR and PMR spectra) with the photo-adduct of 1,2-naphthoquinone and decanal.

Synthesis of 3-Chloro-4-acetyl-1,2-naphthoquinone. 4-Acetyl-1-naphthol (930 mg, 5 mmol) was dissolved in acetone (100 ml) and added to a solution of Fremy's salt (3 g) dissolved in water (200 ml) and M/6 KH_2PO_4 solution (50 ml). The solution became red after 30 min and an oily substance was separated. The solution was extracted with chloroform (70 ml×3), then the extract was washed with water and dried (Na_2SO_4). After the solvent was removed, the quinone was solidified. 4-Acetyl-1,2-naphthoquinone: red crystals from alcohol, mp 92—93 °C. Yield was theoretical. Dry chlorine was passed into the mixture of 4-acetyl-1,2-naphthoquinone (193 mg) and acetic acid (1.6 g) until the quinone was dissolved. Hot water (80—90 °C) was added into the reaction mixture, then the 3-chloro-4-acetyl-1,2-naphthoquinone which separated was collected and washed with water: reddish orange needles from chloroform, mp 194—197 °C. Its IR and PMR spectra were identical with the data of the corresponding quinone obtained from the photo-induced reaction of 3-chloro-1,2-naphthoquinone with acetaldehyde.

Auto-oxidation of 3-Chloro-4-acetyl-1,2-naphthalenediol The reduction of 3-chloro-4-acetyl-1,2-naphthoquinone with sodium hydrosulfite gave 3-chloro-4-acetyl-1,2-naphthalenediol. This was oxidized into the original quinone in benzene or through a silica gel column.

Photo-addition Products of 3-Bromo-1,2-naphthoquinone with Aliphatic Aldehydes. (i) Acetaldehyde: 3-Bromo-1,2-naphthalenediol monoacetate [**5**: R=CH_3, R_1=Br, R_2=R_3=H]: white needles (44 mg, 18.6%), mp 159.5—160.5 °C. IR: ν_{OH} 3310; $\nu_{C=O}$ 1745 cm^{-1}. PMR ($CDCl_3$), δ: 2.47 (s, 3H, CH_3) 7.32—8.23 (m, 6H, aromatic-H+OH). Found: C, 51.11; H, 3.28%. Calcd for $C_{12}H_9BrO_3$: C, 51.27; H, 3.23 %. 3-Bromo-4-acetyl-1,2-naphthoquinone (trace); IR: $\nu_{C=O}$ 1700, 1690 cm^{-1}. 3-Acetyl-1,2-naphthalenediol (4 mg, 2.4%) was identical (IR spectrum) with the photo-adduct of 1,2-naphthoquinone and acetaldehyde.

(ii) Propionaldehyde: 3-Bromo-1,2-naphthalenediol monopropionate [**5**: R=CH_3CH_2, R_1=Br, R_2=R_3=H]: white needles (20 mg, 8.1%), mp 112—114 °C. IR: ν_{OH} 3320 (br); ν_{CH} 2980; $\nu_{C=O}$ 1740 cm^{-1}. PMR($CDCl_3$), δ: 1.37 (t, 3H, CH_3), 2.78 (q, 2H, CH_2), 7.40—8.22 (m, 6H, aromatic-H). Found: C, 53.08; H, 3.87%. Calcd for $C_{13}H_{11}BrO_3$: C, 52.91; H, 3.76%. 3-Propionyl-1,2-naphthalenediol (15 mg, 8.3%) was identical (IR and PMR spectra) with the photo-adduct of 1,2-naphthoquinone and propionaldehyde.

(iii) Butyraldehyde: 3-Bromo-1,2-naphthalenediol monobutyrate [**5**: R=$CH_3(CH_2)_3$, R_1=Br, R_2=R_3=H]: white crystals (28 mg, 10.8%), mp 126—128 °C. IR: ν_{OH} 3360; ν_{CH} 2970, 2940, 2880; $\nu_{C=O}$ 1740 cm^{-1}. PMR($CDCl_3$), δ: 1.12 (t, 3H, CH_3), 1.90 (sex, 2H, CH_2), 2.72 (t, 2H, $COCH_2$), 7.32—8.00 (m, 6H, aromatic-H+OH). Found: C, 54.22; H, 4.21%. Calcd for $C_{14}H_{13}BrO_3$: C, 54.39; H, 4.24%. 3-Butyryl-1,2-naphthalenediol (8 mg, 4.2%) was identical (IR spectrum) with the photo-adduct of 1,2-naphthoquinone and butyraldehyde.

(iv) Isobutyraldehyde: 3-Bromo-1,2-naphthalenediol monoisobutyrate [**5**: R=$(CH_3)_2CH$, R_1=Br, R_2=R_3=H]: white needles (38 mg, 14.7%), mp 106—107 °C. IR: ν_{OH} 3380 (br); ν_{CH} 2980, 2940, 2880; $\nu_{C=O}$ 1730 cm^{-1}. PMR($CDCl_3$), δ: 1.41 (d, 6H, $(CH_3)_2$), 1.44 (d, 6H, $(CH_3)_2$), 2.95 (sep, 1H, CH), 2.98 (sep, 1H, CH), 7.24—8.20 (m, 12H, aromatic-H +OH). Found: C, 54.15; H, 4.12%. Calcd for $C_{14}H_{13}BrO_3$: C, 54.39; H, 4.24%. 3-Butyryl-1,2-naphthalenediol (10 mg, 5.2%) was identical (IR spectrum) with the photo-adduct of 1,2-naphthoquinone and isobutyraldehyde.

(v) Valeraldehyde: 3-Bromo-1,2-naphthalenediol monovalerate [**5**: R=$CH_3(CH_2)_3$, R_1=Br, R_2=R_3=H]: white needles (69 mg, 25.5%), mp 96—97 °C. IR: ν_{OH} 3250 (br); ν_{CH} 2965, 2935, 2870; $\nu_{C=O}$ 1728 cm^{-1}. PMR(CCl_4), δ: 0.88 —1.90 (m, 7H, $CH_3(CH_2)_2$), 2.60 (t, 2H, $COCH_2$), 6.61 (1H, OH), 7.30—8.10 (m, 5H, aromatic-H). Found: C, 55.55; H, 4.49%. Calcd for $C_{15}H_{15}BrO_3$: C, 55.75; H, 4.68%. 3-Bromo-4-valeryl-1,2-naphthoquinone: orange needles (8 mg, 3%), mp 141—142 °C. IR: ν_{CH} 2965, 2935, 2880; $\nu_{C=O}$ 1700, 1685 cm^{-1}. PMR(CCl_4), δ: 0.96 (t, 3H, CH_3), 1.30—1.80 (m, 4H, $(CH_2)_2$), 2.78 (t, 2H, $COCH_2$), 6.94—8.08 (m, 4H, aromatic-H). Found: C, 56.13; H, 4.21%. Calcd for $C_{15}H_{13}BrO_3$: C, 56.10; H, 4.08%. 3-Valeryl-1,2-naphthalenediol (18 mg, 8.8%) was identical (IR spectrum) with the photo-adduct of 1,2-naphthoquinone and valeraldehyde.

(v) Isovaleraldehyde: 3-Bromo-1,2-naphthalenediol monoisovalerate [**5**: R=$(CH_3)_2CHCH_2$, R_1=Br, R_2=R_3=H]: white needles (59 mg, 21.8%), mp 124.5—125.5 °C. IR: ν_{OH} 3335; ν_{CH} 2960, 2877; $\nu_{C=O}$ 1735 cm^{-1}. PMR($CDCl_3$), δ: 1.10 (d, 6H, $(CH_3)_2$), 1.13 (d, 6H, $(CH_3)_2$), 2.30 (m, 2H, CH), 2.54 (d, 2H, $COCH_2$), 2.57 (d, 2H, $COCH_2$), 5.60 (1H, OH), 5.90 (1H, OH), 7.23—8.20 (m, 10H, aromatic-H). Found: C, 55.68; H, 4.62%. Calcd for $C_{15}H_{15}BrO_3$: C, 55.75; H, 4.68%. 3-Bromo-4-isovaleryl-1,2-naphthoquinone: orange crystals (6 mg, 2.2%), mp 151—153 °C. IR: ν_{CH} 2975, 2885; $\nu_{C=O}$ 1700, 1685 cm^{-1}. PMR(CCl_4), δ: 1.14 (d, 6H, $(CH_3)_2$), 2.35 (m, 1H, CH), 2.65 (d, 2H, $COCH_2$), 6.95—8.09 (m, 4H, aromatic-H). 3-Isovaleryl-1,2-naphthalenediol (14 mg, 6.8%) was identical (IR and PMR spectra) with the photo-adduct of 1,2-naphthoquinone and isovaleraldehyde.

(vii) Hexanal: 3-Bromo-1,2-naphthalenediol monohexanoate [**5**: R=$CH_3(CH_2)_4$, R_1=Br, R_2=R_3=H]: white needles (57 mg, 20.1%), mp 89.5—90.5 °C. IR: ν_{OH} 3250; ν_{CH} 2950, 2875; $\nu_{C=O}$ 1730 cm^{-1}. PMR(CCl_4), δ: 0.92 (t, 3H, CH_3), 1.20—1.90(m, 6H, $(CH_2)_3$), 2.60(t, 2H, $COCH_2$), 6.10(1H, OH), 7.32—8.16(m, 5H, aromatic-H). Found: C, 56.83; H, 5.19%. Calcd for $C_{16}H_{17}BrO_3$: C, 56.99; H, 5.08%. 3-Bromo-4-hexanoyl-1,2-naphthoquinone: orange plates (7 mg, 2.5%), mp 100—101 °C. IR: ν_{CH} 2970, 2946, 2878; $\nu_{C=O}$ 1703, 1683 cm^{-1}. PMR(CCl_4), δ: 0.93(t, 3H, CH_3), 1.27—1.88(m, 6H, $(CH_2)_3$), 2.81(t, 2H, $COCH_2$), 6.87—8.04(m, 4H, aromatic-H). 3-Hexanoyl-1,2-naphthalenediol (15 mg, 6.9%) was identical(IR and PMR spectra) with the photo-adduct of 1,2-naphthoquinone and hexanal.

(viii) Heptanal: 3-Bromo-1,2-naphthalenediol monohexanoate[**5**: R=$CH_3(CH_2)_5$, R_1=Br, R_2=R_3=H]: white needles (30 mg, 10.2%), mp 78.5—79.5 °C. IR: ν_{OH} 3375; ν_{CH} 2958, 2940, 2860; $\nu_{C=O}$ 1725 cm^{-1}. PMR(CCl_4), δ : 0.94—1.88(br. m, 11H, $CH_3(CH_2)_4$), 2.62(t, 2H, $COCH_2$), 6.06 (1H, OH), 7.30—8.20(m, 5H, aromatic-H). Found: C, 58.24; H,5.44%. Calcd for $C_{17}H_{19}BrO_3$: C,58.13; H, 5.45%. 3-Heptanoyl-1,2-naphthalenediol(17 mg, 7.5%) was identical(IR and PMR spectra) with the photo-adduct of 1,2-naphthoquinone and heptanal.

(ix) Octanal: 3-Bromo-1,2-naphthalenediol monooctanoate[**5**: R=$CH_3(CH_2)_6$, R_1=Br, R_2=R_3=H]: white needles (20 mg, 6.5%), mp 65—66 °C. IR: ν_{OH} 3350(br); ν_{CH} 2930, 2860; $\nu_{C=O}$ 1735 cm^{-1}. PMR(CCl_4), δ: 0.82—1.90(br.m, 26H, $CH_3(CH_2)_5$), 2.64(t, 2H, $COCH_2$), 2.67(t, 2H, $COCH_2$), 5.96(2H, OH), 7.30—8.20(m, 10H, aromatic-H). Found: C,59.16; H,5.85%. Calcd for $C_{18}H_{21}BrO_3$: C, 59.19; H, 5.79%. 3-Octanoyl-1,2-naphthalenediol (5 mg, 2.1%) was identical(IR spectrum) with the photo-adduct of 1,2-naphthoquinone and octanal.

(x) Nonanal: 3-Bromo-1,2-naphthalenediol mononononanoate[**5**: R=$CH_3(CH_2)_7$, R_1=Br, R_2=R_3=H]: white needles (27 mg, 8.5%), mp 82—83 °C. IR: ν_{OH} 3275(br); ν_{CH} 2925, 2860; $\nu_{C=O}$ 1735 cm^{-1}. PMR(CCl_4), δ: 0.82—1.95

(br. m, 15H, $CH_3(CH_2)_6$), 2.66(t, 2H, $COCH_2$), 5.99(s, 1H, OH), 7.33—8.23 (m, 5H, aromatic-H). Found: C, 60.33; H, 6.10%. Calcd for $C_{19}H_{23}BrO_3$: C,60.17; H, 6.11%. 3-Bromo-4-nonanoyl-1,2-naphthoquinone: orange crystals (8 mg 2.5%), mp 87—88 °C. IR: ν_{CH} 2945,2870; $\nu_{C=O}$ 1715, 1675 cm^{-1}. PMR(CCl_4), δ: 0.86(t, 3H, CH_3), 1.29—1.90(br. m, 12H, $(CH_2)_6$), 2.76(t, 2H, $COCH_2$), 6.93—8.08(m, 4H, aromatic-H). Found: C,60.25; H,5.50%. Calcd for $C_{19}H_{21}BrO_3$: C, 60.49; H, 5.61%. 3-Nonanoyl-1,2-naphthalenediol(9 mg, 3.6%) was identical (IR spectrum) with the photo-adduct of 1,2-naphthoquinone and nonanal.

(xi) Decanal: 3-Bromo-1,2-naphthalenediol monodecanoate [**5**: $R=CH_3(CH_2)_8$, $R_1=Br$, $R_2=R_3=H$]: white needles (28 mg, 8.5%), mp 79—80 °C. IR: ν_{OH} 3250(br); ν_{CH} 2960, 2920, 2858; $\nu_{C=O}$ 1728 cm^{-1}. PMR(CCl_4), δ: 0.80—1.95(br. m, 17H, $CH_3(CH_2)_7$), 2.62 (t, 2H, $COCH_2$), 6.19(1H, OH), 7.30—8.10(m, 5H, aromatic-H). Found: C, 60.94; H, 6.44%. Calcd for $C_{20}H_{25}BrO_3$: C,61.08; H,6.41%. 3-Bromo-4-decanoyl-1,2-naphthoquinone: orange plates (10 mg, 3%), mp 89—90 °C. IR: ν_{CH} 2945, 2870; $\nu_{C=O}$ 1715, 1675 cm^{-1}. PMR(CCl_4), δ: 0.88(t, 3H, CH_3), 1.17—1.84 (br. m, 14H, $(CH_2)_7$), 2.84(t, 2H, $COCH_2$), 6.96—8.13 (m, 4H, aromatic-H). Found: C,61.35; H,5.82%. Calcd for $C_{20}H_{23}BrO_3$: C,61.39; H,5.92%. 3-Decanoyl-1,2-naphthalenediol (8 mg, 3%) was identical(IR spectrum) with the photo-adduct of 1,2-naphthoquinone and decanal.

Photo-addition Products of 3-Methyl-1,2-naphthoquinone with Acetaldehyde: 3-Methyl-1,2-naphthalenediol monoacetate [**5**: $R=CH_3$, $R_1=CH_3$, $R_2=R_3=H$]: white crystals (37 mg, 17%), mp 127—128 °C. IR: ν_{OH} 3340(br); $\nu_{C=O}$ 1739 cm^{-1}. PMR($CDCl_3$), δ: 2.28(s, 3H, CH_3), 2.37(s, 3H, CH_3), 2.40(s, 3H, $COCH_3$), 2.46(s, 3H, $COCH_3$), 5.47(1H, OH), 5.60(1H, OH), 7.29—8.15(m, 10H, aromatic-H). Found: C, 72.08; H, 5.59%. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59%. 3-Methyl-4-acetyl-1,2-naphthoquinone: orange crystals (14 mg, 6.5%), mp 180—182 °C. IR: $\nu_{C=O}$ 1700, 1675 cm^{-1}. PMR(CCl_4), δ: 1.90(s, 3H, CH_3), 2.44(s, 3H, $COCH_3$), 6.88—8.05 (m, 4H, aromatic-H). Found: C, 73.03; H, 4.83%. Calcd for $C_{13}H_{10}O_3$: C, 72.89; H, 4.71%.

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