3-ACYL-1,2-NAPHTHOQUINOLS FROM THE PHOTO-INDUCED REACTION
OF 1,2-NAPHTHOQUINONE DERIVATIVES WITH ALIPHATIC ALDEHYDES

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3-Acyl-1,2-naphthoquinols and 1,2-naphthoquinol monoacylesters were produced in the photochemical reactions of 1,2-naphthoquinones with a variety of aliphatic aldehydes. From the photochemical reactions of 3-halogeno-1,2-naphthoquinones with aliphatic aldehydes were obtained also 3-acyl-1,2-naphthoquinols; that is, the same products with those from the photochemical reactions of 1,2-naphthoquinone with aliphatic aldehydes, accompanying with 3-halogeno-1,2-naphthoquinol monoacylesters.

Photochemical reaction of o-quinones(1),i.e. phenanthraquinone¹⁻⁸⁾ or o-benzoquinone⁹⁾ with aldehydes have been examined by many investigators to give 1,2-endiol monoesters ((2); O-acylated compound) and their cyclic acetal(3) as shown in the following:

According to Awad and Hafez 4-cyano-1,2-naphthoquinone, however, has been reported to behave differently in the photo-induced reaction with aliphatic aldehydes to give the corresponding 3-acylated quinol(C-acylated compound), whereas in the reaction with aromatic aldehydes the usual endiol monoesters were obtained. They have concluded that for the attaking of acyl group to ring carbon a strong electron attracting group such as cyano group should be present in the ring.

On the contrary to their opinion the present authors have found that in the photo-induced reaction of 1,2-naphthoquinone with aliphatic aldehydes acylated 1,2-naphthoquinols at ring carbon could be obtained, and that a part of halogen atom of 3-halogeno-1,2-naphthoquinone derivatives can be substituted by acyl group to give

3-acyl-1,2-naphthoquinols. In this work the reaction of 1,2-naphthoquinone(Ia), 6-bromo-1,2-naphthoquinone(Ib), 6-methyl-1,2-naphthoquinone(Ic), 4-cyano-1,2-naphthoquinone(Id), 3-chloro-1,2-naphthoquinone(Va), and 3-bromo-1,2-naphthoquinone(Vb) with aliphatic aldehydes were investigated. A typical experimental procedure was the following; 1,2-naphthoquinone(1.3 mmol) and acetaldehyde(10 mmol) were dissolved in benzene(25 ml) and irradiated in a usual glass tube by 300W high pressure Hg arc lamp through 5 cm thick of water layer. After irradiation for 3-7 days long the reaction mixture was concentrated under a reduced pressure at room temperature, and then the residue was chromatographed on silica gel column. Elution with benzene afforded 60 mg of orange crystal, mp 135-136°C and 100 mg of white crystal, mp 136-138°C.

Scheme A

The structure of the orange crystal was assigned to (Π a) on the basis of the following data. Elemental analysis; found, C:71.07, H:4.99%; calcd. for $C_{12}H_{10}O_3$, C:71.28, H:4.98%. Pmr spectrum; δ (CCl₄):2.76(s,3H,COCH₃), 5.91(s,1H,1-OH,removed by D_2O), 11.48(s,1H, 2-OH,removed by D_2O), 7.18-8.08(m,5H,aromatic protons). Ir spectrum(KBr); $v_{C=O}=1652$, $v_{OH}=3440$ cm⁻¹. Pmr signal at δ :11.48 and these two ir absorption bands indicated the presence of the intramolecularly hydrogen donded carbonyl and hydroxyl groups. Acetylation of (IIa) gave 1,2-diacetoxy-3-acetylnaphthalene; mp 155-157 °C. Ir(KBr); $v_{C=O}=1687$, 1770 cm⁻¹. Pmr; δ (CDCl₃):2.37(s,3H,-OCOCH₃), 2.46(s,3H,-OCOCH₃), 2.67(s,3H,3-COCH₃), 7.28-8.18(m,5H,aromatic protons). Methylation of (IIa) with dimethyl sulfate in alkaline solution gave 1-methoxy-2-hydroxy-3-acetylnaphthalene, pale yellow crystal; mp 80-81 °C. Ir(KBr); $v_{OH}=3420$, $v_{C=O}=1655$ cm⁻¹. Pmr; δ (CCl₄):2.78(s,3H,3-COCH₃), 4.06(s,3H,1-OCH₃), 11.42(s,1H, 2-OH,removed by D_2O), 7.16-8.05(m, 5H, aromatic protons). Again, these evidences indicate the presence of strongly and intramolecularly hydrogen bonded carbonyl and hydroxyl groups. From the results described above the orange photo-

addition product should be assigned to structure(IIa). The another white crystal having mp 136-138 °C was confirmed to be the mixture of two isomeric endiol monoesters(IIIa and IVa; mixing ratio, IIIa/IVa \simeq 1/1) on the following bases. Ir(KBr); $v_{OH}=3400$, $v_{C=O}=1743$ cm⁻¹. Pmr spectrum; δ (CDCl₃):2.40(s,3H,-OCOCH₃), 2.52(s,3H,-OCOCH₃), 7.13-7.88(m,14H, aromatic and OH protons). Acetylation of the crystal gave 1,2-diacetoxynaphthalene; mp 108-111 °C, identical with authentic sample 12) by means of mixed melting point determination, ir, and pmr.

The similar C-acylated products and endiol monoesters were obtained in the photo-chemical reactions of 4-cyano-1,2-naphthoquinone, 6-bromo-1,2-naphthoquinone and 6-methyl-1,2-naphthoquinone with aliphatic aldehydes (Scheme A). Thus, we can conclude that the ring C-acylation of 1,2-naphthoquinone derivatives is of essential in the photochemical reaction of 1,2-naphthoquinone derivatives with aliphatic aldehydes.

Moreover, 3-chloro- and 3-bromo-1,2-naphthoquinone gave the same C-acylated product in the photochemical reaction with aliphatic aldehydes, although their yield are not so high. For example, irradiation of 3-chloro-1,2-naphthoquinone and acetaldehyde in benzene afforded the mixture of 3-chloro-1,2-naphthoquinol monoacetylester (ca. 50%), 3-acetyl-1,2-naphthoquinol (2-3%); i.e., the same product obtained from the reaction of 1,2-naphthoquinone with acetaldehyde, and a large amount of paraldehyde. Polymerization of acetaldehyde to paraldehyde suggests the formation of hydrogen chloride in the reaction mixture. Analogous substituted products at position 3 by acyl group were constantly obtained in the photochemical reactions of 3-halogeno-1,2-naphthoquinones with the other aliphatic aldehydes(Scheme B). No rearrangement of the O-acylated monoesters to C-acylated quinols was confirmed under the same photochemical condition.

Scheme B

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