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

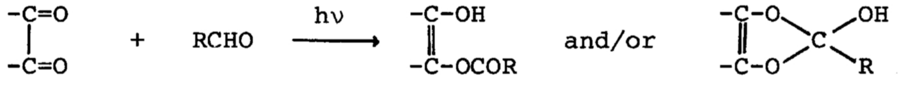
Kazuhiro MARUYAMA* and Akio TAKUWA**

* Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606

** Department of Chemistry, Faculty of Literature and Science, Shimane University, Matsue 690

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-benzoquinone,9) 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:

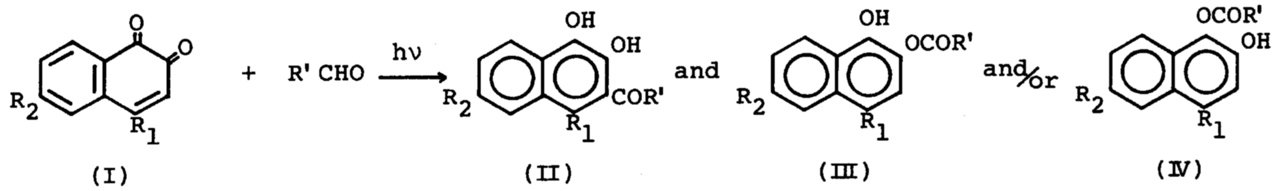


(1) (2) (3)

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.10) 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.



a : R_1=H R_2=H
b : R_1=H R_2=Br
c : R_1=H R_2=CH_3
d : R_1=CN R_2=H

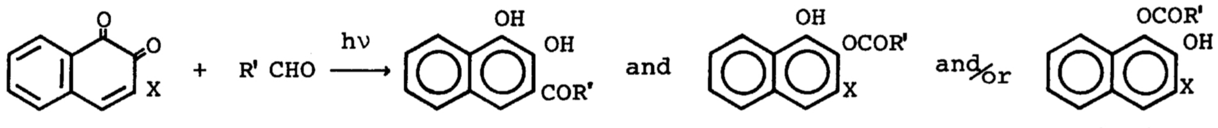
R' = CH_3-
C_2H_5-
n-C_3H_7-
iso-C_3H_7-

Scheme **A**

The structure of the orange crystal was assigned to (IIa) 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 (CCl_4):2.76(s,3H,$COCH_3$), 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);$\nu_{C=O}$= 1652, ν_{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); $\nu_{C=O}$=1687, 1770 cm^{-1}. Pmr; δ ($CDCl_3$):2.37(s,3H,-$OCOCH_3$), 2.46(s,3H,-$OCOCH_3$), 2.67(s,3H,3-$COCH_3$), 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);ν_{OH}=3420, $\nu_{C=O}$=1655 cm^{-1}. Pmr; δ (CCl_4):2.78(s,3H,3-$COCH_3$), 4.06(s,3H,1-OCH_3), 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 photoaddition 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 ≃ 1/1) on the following bases. Ir(KBr); ν_{OH}=3400, $\nu_{C=O}$=1743 cm^{-1}. Pmr spectrum; δ (CDCl$_3$):2.40(s,3H,-OCOCH$_3$), 2.52(s,3H, -OCOCH$_3$), 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 photochemical 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.



(V) (IIa) (VI) (VII)

a : X=Cl
b : X=Br

R' = CH$_3$-, C$_2$H$_5$-
n-C$_3$H$_7$-, iso-C$_3$H$_7$-

Scheme **B**

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