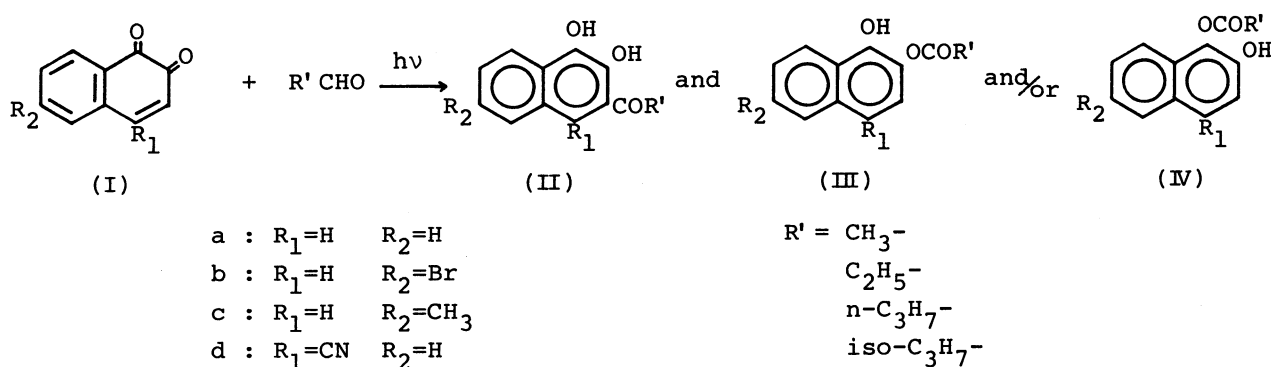




3-acyl-1,2-naphthoquinols. In this work the reaction of 1,2-naphthoquinone (Ia), 6-bromo-1,2-naphthoquinone (Ib), 6-methyl-1,2-naphthoquinone (Ic), 4-cyano-1,2-naphthoquinone (Id), 3-chloro-1,2-naphthoquinone (Va), and 3-bromo-1,2-naphthoquinone (Vb) with aliphatic aldehydes were investigated. A typical 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 (IIa) on the basis of the following data. Elemental analysis; found, C:71.07, H:4.99%; calcd. for C<sub>12</sub>H<sub>10</sub>O<sub>3</sub>, C:71.28, H:4.98%. Pmr spectrum;  $\delta$  (CCl<sub>4</sub>): 2.76 (s, 3H, COCH<sub>3</sub>), 5.91 (s, 1H, 1-OH, removed by D<sub>2</sub>O), 11.48 (s, 1H, 2-OH, removed by D<sub>2</sub>O), 7.18-8.08 (m, 5H, aromatic protons). Ir spectrum (KBr);  $\nu_{C=O}$  = 1652,  $\nu_{OH}$  = 3440 cm<sup>-1</sup>. Pmr signal at  $\delta$ : 11.48 and these two ir absorption bands indicated the presence of the intramolecularly hydrogen bonded 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<sup>-1</sup>. Pmr;  $\delta$  (CDCl<sub>3</sub>): 2.37 (s, 3H, -OCOCH<sub>3</sub>), 2.46 (s, 3H, -OCOCH<sub>3</sub>), 2.67 (s, 3H, 3-COCH<sub>3</sub>), 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);  $\nu_{OH}$  = 3420,  $\nu_{C=O}$  = 1655 cm<sup>-1</sup>. Pmr;  $\delta$  (CCl<sub>4</sub>): 2.78 (s, 3H, 3-COCH<sub>3</sub>), 4.06 (s, 3H, 1-OCH<sub>3</sub>), 11.42 (s, 1H, 2-OH, removed by D<sub>2</sub>O), 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-



## References

- 1) H. Klinger, *Annalen.*, 249, 137 (1888); 382, 211 (1911).
- 2) A. Schönberg and R. Moubasher, *J. Chem. Soc.*, 1939, 1430.
- 3) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 1949, 997.
- 4) A. Mustafa, A.H.E. Harhash, A.K.E. Monsour and S.M.A.E. Omuran, *J. Amer. Chem. Soc.*, 78, 4306 (1956).
- 5) A. Mustafa, *J. Chem. Soc.*, 1951, 1034.
- 6) R.F. Moore and W.A. Waters, *J. Chem. Soc.*, 1953, 238.
- 7) M.B. Rubin and P. Zwickowits, *J. Org. Chem.*, 29, 2362 (1964).
- 8) K. Maruyama, A. Takuwa, T. Otsuki and S. Kako, *Bull. Inst. Chem. Res., Kyoto Univ.*, 50, 348 (1972).
- 9) A. Schönberg, N. Latif, R. Moubasher and Sina, *J. Chem. Soc.*, 1951, 1364.
- 10) A. Schönberg, W.I. Awad and G.A. Mousa., *J. Amer. Chem. Soc.*, 77, 3850 (1955).
- 11) W.I. Awad and M.S. Hafez, *J. Amer. Chem. Soc.*, 80, 6057 (1957).
- 12) Korn, *Ber.*, 17, 3025 (1884).

(Received March 8, 1974)