CHEMISTRY LETTERS, pp.719-720, 1974. Published by the Chemical Society of Japan

PHOTO-INDUCED ISOMERIZATION OF 2-ACYL-3-METHYL-1,4-NAPHTHOQUINONE-2,3-EPOXIDE

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2-Acyl-3-methyl-1,4-naphthoquinone-2,3-epoxide(1) isomerizes photochemically to give lactone. The spectral data and chemical reactions of the lactone are compatible with structure(2). Photochemical reaction of (1) with xanthene was also described.

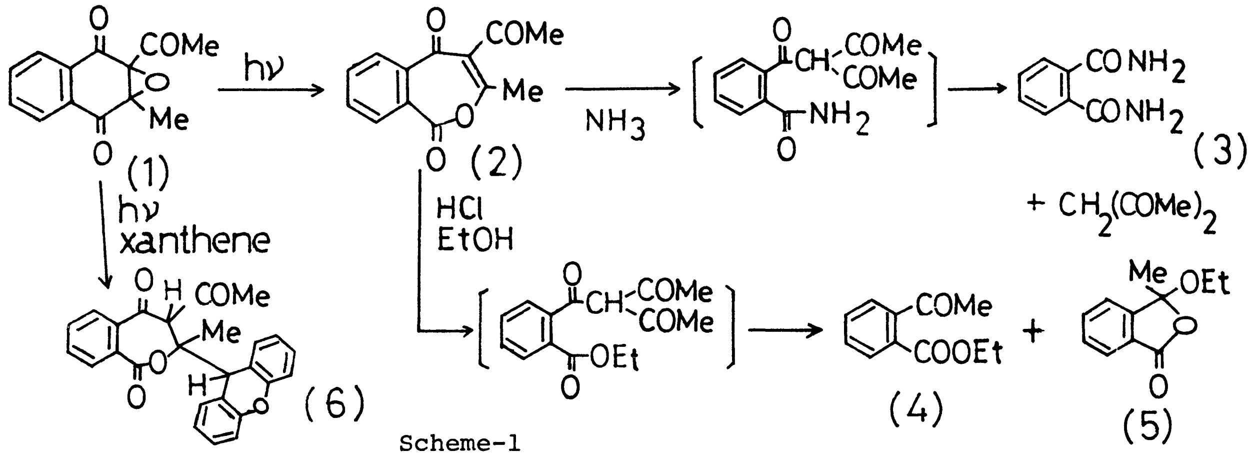
Photo-isomerizations of cyclopentenone oxides[1)] or indenone oxides[2)] are well known, but no report on the photo-induced isomerization of quinone epoxides has been published. We shall report here on the photo-isomerization of 2-acyl-3-methyl-1,4-naphthoquinone-2,3-epoxide.

2-Acyl-3-methyl-1,4-naphthoquinone-2,3-epoxide(1)(100 mg) was dissolved in benzene or acetonitrile(30 ml) and irradiated in a glass tube by high pressure Hg-arc lamp(300 W) for 8 hours. A photo-product was isolated from the reaction mixture by usual work-up. The photo-product was white needles, mp 133-134 °C, after recrystallization from hexane-benzene (yield 31% in benzene, and 45% in acetonitrile). The structure of the photo-product was assigned to structure(2) as determined by the following methods;

Elemental analysis; found. C:67.72, H:4.23%, calcd. for $C_{13}H_{10}O_4$.C:67.82, H:4.38%. Mass spectrum; m/e 230(M^+), 188(M^+ - CH_2=C=O), 173(188 - CH_3). Ir spectrum indicated the existence of three carbonyl groups, $\nu_{C=O}$=1795(lactone), 1705(acetyl group), 1650 cm^{-1}. Uv spectrum; λ_{max}= 245, 283, 314 nm (logε = 4.12, 4.20, 4.10) (solvent:$CHCl_3$). Pmr spectrum; δ=2.49(3H, methyl, singlet), 2.70(3H, acetyl group, singlet), 7.5-8.0(4H, aromatic, multiplet) ppm (solvent:$CDCl_3$).

Furthermore, a positive iodoform test of the photo-product indicates the existence of acetyl group. When the absolute ethanol solution of the photo-product was saturated with dry ammonia, it transformed to phthalic acid diamide(3) and acetylacetone, and also the treatment with dry hydrogen chloride gave o-acetylbenzoic acid ethyl ester(4) and 3-methyl-3-ethoxy-phthalide(5)[3)]. The compounds (3)-(5) were identified by their unequivocal syntheses.

Photo-reduction of (1) with xanthene gave a photo-adduct(6), mp 151-151.5 °C, which might be formed by the reaction of the compound(2) with xanthyl radical.

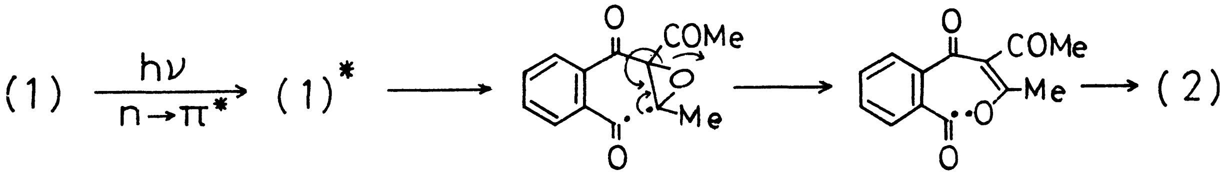


Scheme-1

The structure of the photo-adduct was assigned to (6) by its ir, nmr spectra and elemental analysis.

The chemical reactions described above substantiate the assignment of structure(2) to the photo-isomerization product of (1), and the reaction courses can be summarized in Scheme-1.

A similar isomerization occurs in the photochemical reaction of 2-propionyl-3-methyl-1,4-naphthoquinone-2,3-epoxide even in a lower yield (10-15%), but no reaction in 2-acetyl-1,4-naphthoquinone-2,3-epoxide case. The reaction course of the photo-isomerization of (1) may be formulated as follows;



The photochemical reaction of alkyl substituted 1,4-naphthoquinone-2,3-epoxides are likely to proceed by other pathways, which is now under investigation.

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(Received May 24, 1974)