PHOTOCHEMICAL REACTION OF 6-ALKOXY-7-(2-OXOALKYL)-QUINOLINE-5,8-QUINONES

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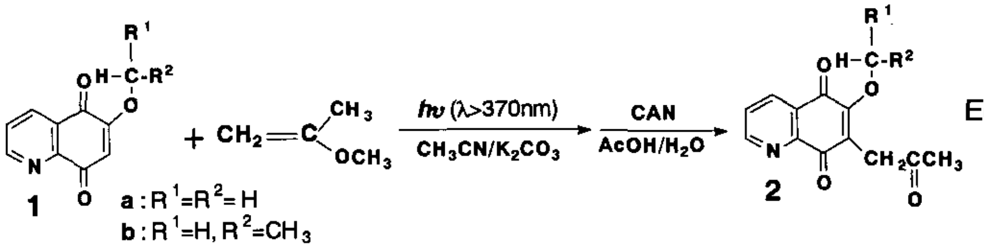
Abstract- Photochemical reaction of 6-alkoxy-7-(2-oxoalkyl)quinoline-5,8-quinones in benzene gave a novel heterocyclic quinones, 2-alkyl-4-methylquino[6,7-d]-[1,3]dioxepine-6,11-diones *via* intramolecular γ-H-abstraction.

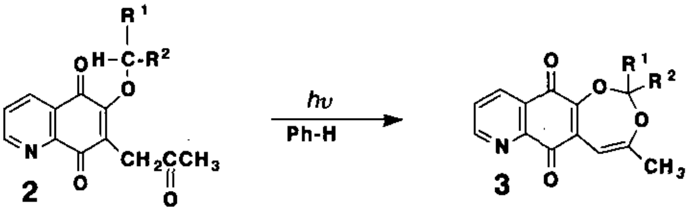
Heterocyclic quinones have attracted considerable interests from both biological and photochemical view points.[1] Among these, synthetic studies of quinones containing the quinoline-5,8-quinone moiety like streptonigrin, lavendamycin, and streptonigrone have been extensively investigated[2] while very little work has been done on the introduction of heterocyclic ring to the quinoline-5,8-quinone moiety. Recently, we have developed a photochemical introduction of 1,3-dioxepine[3] and 1,3-oxathiepine[4] ring into naphthoquinone nuclei. In continuation with these studies, we now report here that the synthesis of 6-alkoxy-7-(2-oxoalkyl)quinoline-5,8-quinones (**2**) and photochemical reaction of **2** in benzene gave the heterocycle-fused quinoline-5,8-quinone (**3**).
The title compounds (**2**)[5] were prepared in 77% (**2a**) and 70% (**2b**) resp. by the photochemical reaction of the corresponding 6-alkoxyquinoline-

5,8-quinones (1)[6] with 2-methoxypropene in acetonitrile with a $CuSO_4$ filtered light from 400 W high-pressure Hg lamp in the presence of potassium carbonate under a nitrogen and subsequent cerium(IV) ammonium nitrate (CAN) oxidation of the photo-products in aqueous acetic acid.[3]



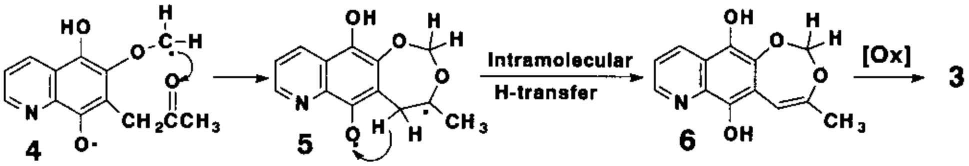
Eq. 1

Irradiation of a benzene solution of **2a** (1.6×10^{-4} mol dm^{-3}) with a Pyrex-filtered light from 400W high-pressure Hg lamp under a nitrogen for 3 h gave a novel cyclization product, 4-methylquino[6,7-d][1,3]-dioxepine-6,11-dione (**3a**) in 15% yield with 92% conversion of **2a**. The structure of **3a** was assigned on the basis of its spectroscopic analysis.[7] The uv spectrum of **3a** in dichloromethane showed a characteristic *band at 450 nm due to 1,3-dioxepin ring-fused quinoline-5,8-quinone, in* analogy with 1,3-dioxepin ring-fused 1,4-naphthoquinone.[3]



Eq. 2

Similarly, irradiation of **2b** gave the cyclized product (**3b**) in 60% yield with 86% conversion of **2b**. Photochemical reactivity increased in order of **2a** < **2b** which reflected the γ-C-H bond strength. The photoreaction of **2** was sensitized by xanthene, but efficiently quenched by anthracene, indicating that these photoreaction occurred from their triplet excited state. Accordingly, a plausible mechanism for the formation of 3 is given in Scheme 1. Photocylization may begin with intramolecular γ-H-abstraction[8] by the quinone carbonyl of **2** to give a biradical (**4**), which then cyclizes to (**5**). Intramolecular disproportionation of the biradical (5) produces hydroquinone (**6**), which is oxidized by the unreacted quinone(2)[9] or air, to give 3.



Scheme 1

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5. *7-Acetonyl-6-methoxyquinoline-5,8-quinone (**2a**)*
mp 115 °C; ^{1}H Nmr (90 MHz, $CDCl_3$) δ: 2.30 (s, 3H), 3.80 (s, 2H), 4.17 (s, 3H), 7.63 (dd, J= 8.0, 4.0 Hz, 1H), 8.63 (dd, J= 8.0, 1.80 Hz, 1H), 9.00 (dd, J= 4.0, 1.80 Hz, 1H); ir (KBr)ν_{max}: 1713, 1678, 1622, 1578, 1158 and 1100 cm^{-1}; uv(λ_{max}, nm (ε), CH_2Cl_2) 245 (15500), 362 (1200); GCms (m/z): 247(M^++2H), 203(100%). *Anal.* Calcd for $C_{13}H_{11}NO_4$: C, 63.66; H, 4.52; N, 5.71. Found: C, 63.39; H, 4.38; N, 5.64.
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7. *4-Methylquino[6,7-d][1,3]dioxepine-6,11-dione (**3a**)*
mp 215 °C; ^{1}H Nmr (90 MHz, $CDCl_3$) δ: 2.17 (s, 3H), 5.53 (s, 2H), 6.10 (s, 3H), 7.65 (dd, J= 8.3, 4.8 Hz, 1H), 8.45 (dd, J= 8.1, 1.0 Hz, 1H), 9.00 (dd, J= 4.8, 1.0 Hz, 1H); ir (KBr)ν_{max}: 1682, 1667, 1626, 1568, 1100 cm^{-1}; uv(λ_{max}, nm (ε), CH_2Cl_2) 284 (13200), 449 (2680); ms (m/z): Exact mass: Calcd for $C_{13}H_9NO_4$: 243.0532. Found: 243.0528.
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9. The evidence for existence of hydroquinone of 2 was confirmed by the 400 MHz ^{1}H Nmr spectrum of the photoreaction mixture in benzene-d_6.

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