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PHOTOCHEMICAL REACTION OF 2-ACETYL-1,4-BENZOQUINONE IN THE PRESENCE OF ROSE BENGAL

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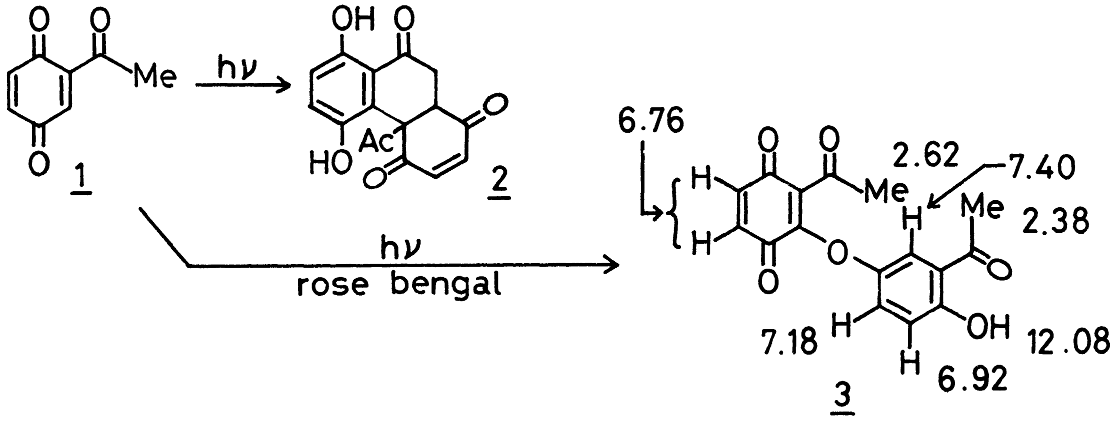
Irradiation of 2-acetyl-1,4-benzoquinone 1 in acetonitrile in the presence of rose bengal afforded the dimer, 2-acetyl-3-phenoxy-1,4-benzoquinone derivative 3. This is quite different from another dimer 2, which is obtained in the photochemical reaction of 1 in the absence of rose bengal.

It has been reported that photolysis of 2-acyl-1,4-quinones afforded a dimerized product in a good yield.1) For example, irradiation of 2-acetyl-1,4-benzoquinone 1 in a carbon tetrachloride solution afforded the dimer 2 in 60% yield. The present communication deals with photochemical novel dimer formation of 1 in the presence of rose bengal.



When an acetonitrile solution(20ml) of 2-acetyl-1,4-benzoquinone 1(2mmol) and rose bengal(0.01mmol) was externally irradiated for 6 h, 1 was thoroughly consumed. After removal of the solvent, the residue was subjected to a short Florisil column chromatography affording a new type of dimer 3 in 60% yield. The structure of 3, red purple needles, mp 120-121 °C(recrystallized from ether), was assigned to 2-acetyl-3-(3-acetyl-4-hydroxyphenoxy)-1,4-benzoquinone by spectroscopic methods.

The product 3 showed the following spectral data. NMR($CDCl_3$, TMS as internal standard)δ=2.38(3H, s), 2.62(3H, s), 6.76(2H, s), 6.92(1H, d, J=8Hz), 7.18(1H, dd, J= 8 and 2Hz), 7.40(1H, d, J=2Hz), and 12.08(1H, s); IR(KBr disk) 3360, 3060, 1700, 1670, 1620, 1585, 1180, and 1090 cm^{-1}; UV_{max}(CH_3CN)(ε) 440(sh)(860), 346(4200), 250(21600), and 223 nm(21600); MS, m/e(rel intensity), 300(M^+, 40), 151(100), and 149(65). Other 2-acyl-1,4-benzoquinones(propionyl and butyloyl) were found to give similar types of the dimer 3 on irradiation under the same conditions.

This type of photochemical reaction was brought about on irradiating with the longer wavelength light than 480 nm, in which region 1 had no absorption. Although without rose bengal irradiation of an acetonitrile solution of 1 with light of longer wavelength than 480 nm gave no sign of the quinone conversion, direct irradiation of 1 with the whole light from a high pressure Hg-lamp gave the dimer 2.

The presence or absence of oxygen in the reacting system gave no influence on the mode of the photochemical dimerization to give 3. Therefore, the presence of singlet oxygen in the reacting solution scarcely affects on the fashion of the reaction.

The lowest triplet energies of 1,4-benzoquinones carrying electron-accepting groups such as dichloro-1,4-benzoquinones are very similar to that of 1,4-benzoquinone itself(ca.52 kcal/mole).2) The triplet energy of 2-acetyl-1,4-benzoquinone 1 may have the value as high as about 53 kcal/mole. As the triplet energy of rose bengal has determined to be 39-42 kcal/mole,3) the triplet energy transfer from the excited rose bengal to 1 seems to be impossible.

A kind of quinone-rose bengal complexation may concern on the dimerization to 3. However, in visible region we could not detect any appearance of new absorption between 1 and rose bengal dissolved in acetonitrile at room temperature. Thus, it can be concluded that in the ground state there is no detectable interaction between 1 and rose bengal in acetonitrile.

It may not be unsound to suppose the formation of a kind of exciplex between 1 and excited rose bengal at a stage of the dimerization reaction, but the true courses of the two dimerization mechanisms to give 3 and 2 still remain obscure.

REFERENCES

1) Y.Miyagi, K.Kitamura, K.Maruyama, and Y.L.Chow, Chem. Lett., 1978, 33.

2) J.M.Bruce, in S.Patai(Ed.), The chemistry of the quinonoid compounds, Wiley-Interscience, 1974, p.465.

3) K.Gollnick, Adv. Photochem., 6, 1, Interscience, New York(1968).

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