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PHOTOOXYGENATION OF FLAVANONOL-RED RELATED COMPOUNDS

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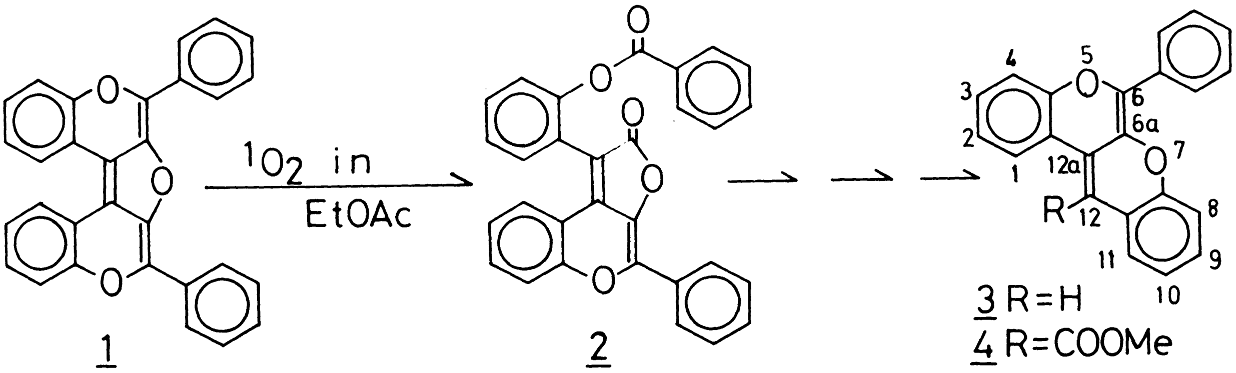
Photooxygenation of 6-phenyl-5,7-dioxa-benz[a]anthracene in ethanol followed by recrystallization from ethanol resulted in the formation of a diethoxy compound by unusual addition of two ethoxyl groups to a C-C double bond. While, recrystallization of the photooxygenation product from methanol afforded a monoethoxy monomethoxy compound.

When 3-hydroxyflavanone was boiled with acetic anhydride and sodium acetate, a red pigment (tentatively named flavanonol-red) was obtained in good yield.[1)] In a previous paper, we reported that the photooxygenation of flavanonol-red 1 afforded photoflavanonol-red 2, and that an orange crystalline compound 3 and a red ester 4 were derived from photoflavanonol-red.[2)] In this paper, we wish to report the photooxygenation of 3 and 4.



1

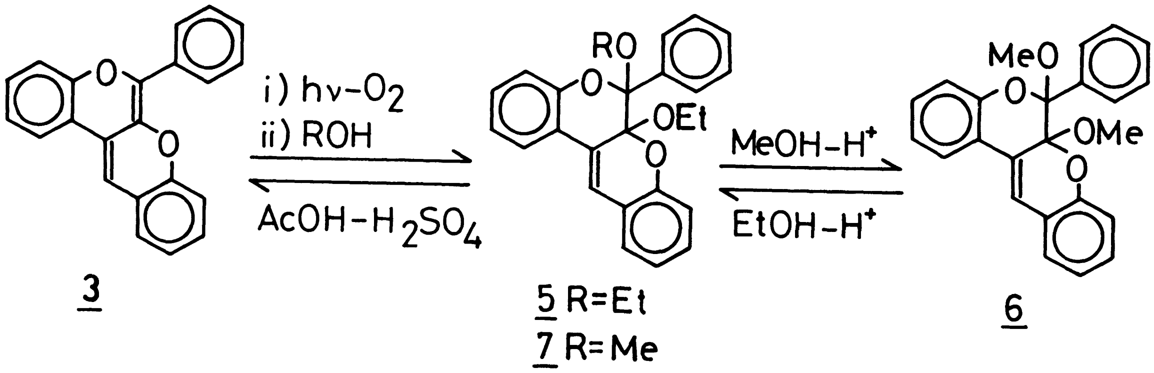
2

3 R=H

4 R=COOMe

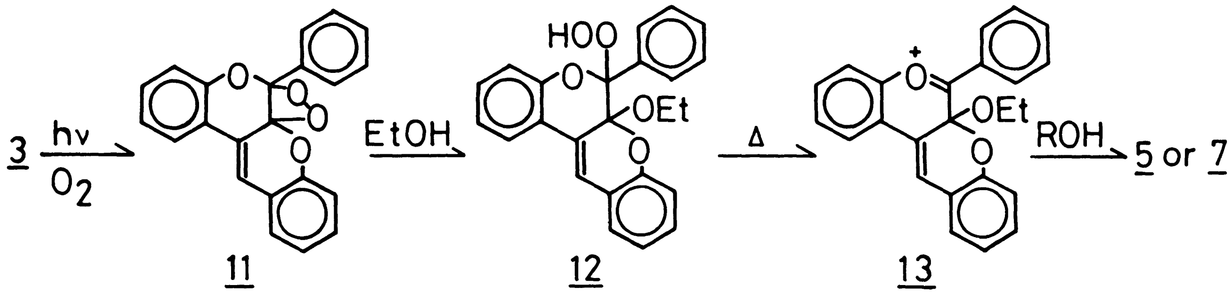
When an orange solution of 3 (200mg) in ethanol (100ml) was irradiated with a sun-light or a 20W fluorescent lamp in the presence of air at ordinary temperature, the orange color faded after a few minutes and an oily material was obtained. Treatment of the oil with ethanol gave a crystalline diethoxy adduct 5, (109mg, 42% yield), $C_{26}H_{24}O_4$, (Found: C, 77.98; H, 6.05%. Calcd for $C_{26}H_{24}O_4$: C, 77.98; H, 6.04%.), m.p. 183-186°C, IR; no absorption in hydroxyl and carbonyl regions, λ_{max}^{EtOH} 239, 294, 332 and 350 nm (log ε 4.40, 4.20, 4.39 and 4.32), ^{1}H nmr ($CDCl_3$) δ 0.8 (t. 3H), 0.9 (t. 3H), 2.9-3.7 (2q. 4H), 6.8-8.2 ppm (m. 14 H), ^{13}C nmr ($CDCl_3$) δ 15.13 (q), 15.28 (q), 58.48 (t), 59.06 (t), 97.90 (s), 101.99 (s), 115.39 (d), 118.03 (d), 118.61 (d), 119.83 (s), 120.27 (s), 121.29 (d), 121.63 (d), 123.59 (s), 123.78 (d), 127.19 (d. 3C by NNE), 128.45 (d), 129.04 (d), 129.37 (d. 2C by NNE), 135.72 (s), 150.72 (s), 153.01 ppm (s). These spectral data shows that 5 is constructed by the addition of two ethoxyl groups to 3. Treatment of 5 with methanol containing one drop of 2M hydrochloric acid gave a dimethoxy adduct 6, $C_{24}H_{20}O_4$, (Found: C, 77.40; H, 5.50 %. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41%.), m.p. 201-203°C, IR; no absorption in hydroxyl and carbonyl regions, λ_{max}^{EtOH} 239, 294, 332 and 350 nm (log ε 4.39, 4.20, 4.39 and 4.32), ^{1}H nmr ($CDCl_3$) δ 2.95 (s. 3H), 3.08 (s. 3H), 6.9-8.1 ppm (m. 14H), ^{13}C nmr ($CDCl_3$) δ 50.73 (q. 2C), 98.24 (s), 101.80 (s), 115.25 (d), 118.12 (d), 119.39 (d), 119.39 (s), 119.97 (s), 121.58 (d), 121.97 (d), 122.46 (s), 123.87 (d), 127.43 (d. 3C by NNE), 128.74 (d), 129.33 (d), 129.67 (d), 129.82 (d. 2C by NNE), 134.50 (s), 150.58 (s), 153.01 ppm (s), which, in turn, quantitatively gave 5 on being boiled in ethanol containing a trace amount of 2M hydrochloric acid. And also 6 was obtained in 40% yield on irradiation of 3 in methanol followed by recrystallization from methanol. From the easy exchange of the alkoxyl groups, it is assumed that the alkoxyl groups in 5 and 6 are the acetal alkoxyl groups. ^{13}C nmr spectra of 5 and 6 show that these compounds contain two alkoxyls, two acetals, one tri-substituted double bond, two di-substituted benzene rings, and a mono-substituted one. Namely, four carbons except for aromatic and alkoxyl carbons were two acetal carbons and two olefinic carbons.

Moreover, the close resemblance of the UV absorption spectral data of 5 and 6 with those of the previously reported compounds 8 and 9 rather than 10 suggests the presence of a stilbene moiety.2,3) Boiling of 5 in acetic acid containing a few drops of conc. sulfuric acid afforded the orange compound 3. By considering the reversibility of these reactions, there seems to be no deep-seated backbone rearrangement. Hence the arrangement of four non-aromatic carbons of 5 appears to be the same as that of 3. These evidence support the structure 5 for the photooxygenation product of 3 in ethanol.



While, the photooxygenation of 3 in ethanol followed by recrystallization from methanol gave a monoethoxy monomethoxy adduct 7, $C_{25}H_{22}O_4$, (Found: C, 77.31 ; H, 5.82%. Calcd for $C_{25}H_{22}O_4$: C, 77.70; H, 5.74%.), m.p. 169-171°C, IR; no absorption in hydroxyl and carbonyl regions, λ_{max}^{EtOH} 239, 294, 332 and 350 nm (log ε 4.29, 4.16, 4.35 and 4.29), ^{1}H nmr ($CDCl_3$) δ 0.83 (t. 3H), 2.95 (s. 3H), 3.35 (q. 2H), 6.8-8.1 ppm (m. 14H). In the previous paper, we reported that the methoxyl group of 9 was observed at δ_{CDCl_3} 3.15 in its ^{1}H nmr spectrum.[2)] The attachment of the methoxyl group of 7 on C-6 was inferred from the comparison of the ^{1}H nmr data of the corresponding methoxyl group in 9.

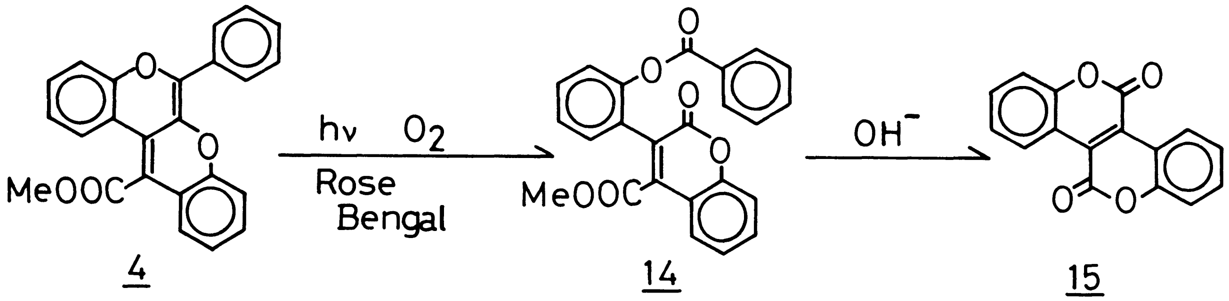
The above photo-products (5, 6 and 7) could not be detected by the photolysis in solvents other than alcohols, nor by photolysis in the alcohols under nitrogen atmosphere.



The formation of 5, 6 and 7 might be explained by the following sequence of reactions; 1) photooxygenation of a C-C double bond (probably the formation of a dioxetane 11), 2) introduction of an alkoxyl group (formation of a hydroperoxide 12), and then 3) thermal decomposition of the hydroperoxide 12 to the dialkoxyl compounds (5, 6 and 7) through a flavylium type intermediate 13.

It may be probable that the stability of the flavylium cation type intermediate 13 contributes to this unusual photooxygenation reaction. The detailed study for this photochemical reaction is now in progress.

The red ester 4 was completely recovered in the photolysis under the same condition described above but the irradiation in the presence of a photosensitizer (Rose bengal) gave a lactone 14, $C_{24}H_{16}O_6$, m.p. 137-139°C, m/e; M^+ 400, ν_{max}^{nujol} 1740, 1720 cm^{-1}, ^1H nmr ($CDCl_3$) δ 3.6 (s. 3H), 7.2-8.1 ppm (m. 13H). Alkaline hydrolysis of 14 gave the dilactone 15 described in the previous paper.[2,4]

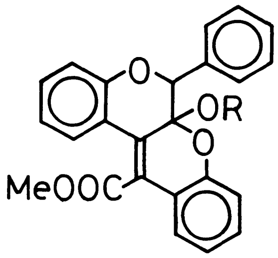


REFERENCES AND NOTE

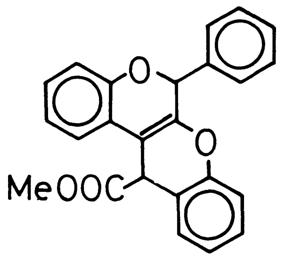
1) T. Kubota, N. Ichikawa, K. Matsuo and K. Shibata, Tetrahedron Lett., 1966, 4671. The detailed description for the revised structure of flavanonol-red 1 will be presented in a full paper.

2) K. Shibata, K. Matsuo, N. Ichikawa and T. Kubota, Chem. Lett., 1979, 511.

3)



8 R=H
9 R=Me



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