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PHOTOOXYGENATION OF FLAVANONOL-RED AND UNUSUAL AUTOXIDATION OF PHOTOFLAVANONOL-RED

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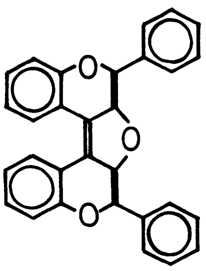
Photooxygenation of flavanonol-red gave photoflavanonol-red by oxidative cleavage of C-C double bond in good yield. In alkaline solution, the autoxidation of photoflavanonol-red afforded 3,4,7,8-dibenzonaphthyrone by unusual oxidative cleavage of C-C double bond.

In the previous paper, we showed that a red pigment was obtained by heating of 3-hydroxyflavanone in acetic anhydride containing anhydrous sodium acetate.[1] (Conveniently, this red pigment was named flavanonol-red.) The structure of flavanonol-red was revised to formula 1 by some degradation reactions, their physical properties, and X-ray crystallography.[2] We would like to report a photooxygenation of flavanonol-red and an autoxidation of the photo-product.

When flavanonol-red was irradiated with sun-light or ultraviolet light in ethyl acetate in the presence of air at ordinary temperature, the red colored solution changed to blue and it gave green crystals, which were named photoflavanonol-red 2, $C_{30}H_{18}O_5$, m.p. 218-220°C, ν_{max} 1750, 1740, 1660, 1620, 1600, 1500, 770 and 765 cm^{-1}, λ_{max}^{EtOH} 234, 315 and 391 nm (log ε 4.65, 4.23 and 4.45), ^1H NMR no peak except in aromatic region (m.). Hydrolysis of 2 with alkali afforded one mole of benzoic acid and one mole of a hydroxy compound 3, $C_{23}H_{14}O_4$, m.p. 275-280°C (decomp.), ν_{max} 3270, 1700 and 1650 cm^{-1}, λ_{max}^{EtOH} 312 and 391 nm (log ε 4.03 and 4.30), which was reconverted to photoflavanonol-red by usual benzoylation. Methylation of 3 with methyl iodide and potassium carbonate in dry acetone gave a monomethyl ether 4, $C_{24}H_{16}O_4$, m.p. 182-183°C, ν_{max} 1740, 1650, 1620 and 1590 cm^{-1}, λ_{max}^{EtOH} 237, 243, 312 and 389 nm (log ε 4.50, shoulder, 4.29 and 4.45), δ_{CDCl_3} 3.90 (s. 3H), 7.00-8.55 ppm (m. 13H). When the hydroxy compound 3 was oxidized with potassium permanganate in dry acetone or with air in a mixture of aqueous sodium hydroxide, tetrahydrofuran and ethanol under refluxing, it afforded benzoic acid and a dilactone 5, $C_{16}H_8O_4$, m.p. 295-296°C, ν_{max} 1725, 1605, 1590, 1310, 1245, 1165, 1110, 775 and 755 cm^{-1}, λ_{max}^{EtOH} 253, 268 and 380 nm (log ε 3.95, 3.92 and 4.10), which was identified by comparison with 3,4,7,8-dibenzonaphthyrone.[3] On ozonization, 4 afforded an anhydride 6, $C_{24}H_{16}O_6$ m.p. 181-183°C, ν_{max} 1860, 1840, 1770 and 1750 cm^{-1}, δ_{CDCl_3} 3.30 (s. 3H), 6.7-8.0 ppm (m. 13H), which was converted to bis(o-methoxyphenyl)maleic anhydride 7, $C_{18}H_{14}O_5$, m.p. 159-160°C, ν_{max} 1820 and 1750 cm^{-1}, δ_{CDCl_3} 3.48 (s. 6H), 6.80-7.6 ppm (m. 8H), by alkaline hydrolysis followed by methylation with dimethyl sulfate and alkali. Anhydride 7 was confirmed through its synthesis from salicylaldehyde methyl ether (see scheme 2). The formation of the anhydride 6 in the above ozonolysis of 4 strongly suggests the formula 2 for photoflavanonol-red.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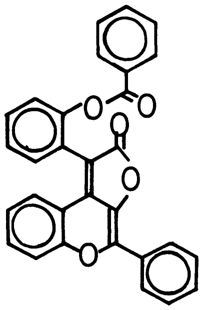
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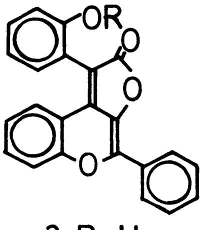
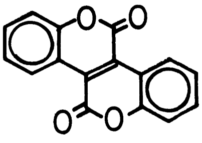

3 R=H
4 R=Me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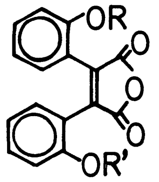
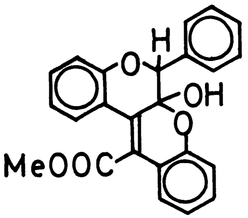


6 R=Me
R'=COPh
7 R=R'=Me

At this point, we studied the autoxidation of the hydroxy compound 3 to the dilactone 5. Treatment of 3 with aqueous sodium hydroxide in refluxing THF and ethanol under nitrogen, followed by esterification with ethereal diazomethane gave a hydroxy ester 8, $C_{24}H_{18}O_5$, m.p. 174-175°C (decomp.), ν_{max} 3500, 1720, 1610 and 1580 cm^{-1}, λ_{max}^{EtOH} 240, 296, 306, 345 and 370 nm (log ε 4.16, 4.03, 3.94, 4.18 and 4.14), δ_{CDCl_3} 3.06 (s. 1H, OH), 3.99 (s. 3H), 5.54 (s. 1H), 6.70-7.90 ppm (m. 13H). Acid treatment of 8 in methanol gave a red crystalline ester 9, $C_{24}H_{16}O_4$, m.p. 151-152°C, ν_{max} 1720, 1640-1550 cm^{-1}(weak five peaks), λ_{max}^{EtOH} 241, 264 and 445 nm (log ε 4.47, 4.41 and 4.05), δ_{CDCl_3} 3.88 (s. 3H), 6.60-8.10 ppm (m. 13H). Catalytic hydrogenation of the red ester 9 with platinum oxide in ethanol afforded a dihydro ester 10, colorless needles, $C_{24}H_{18}O_4$, m.p. 193-195°C, ν_{max} 1730, 1695 (unassignable medium absorption), 1590 cm^{-1}, λ_{max}^{EtOH} 280, 295 and 312 nm (log ε 3.79, 3.77 and 3.93), δ_{CDCl_3} 3.77 (s. 3H), 4.87 (broad s. 1H), 5.97 (broad s. 1H), 6.7-7.9 ppm (m. 13H). From the above spectral data, it was concluded that the catalytic hydrogenation of 9 involved 1,4-hydrogen addition to the diene system of 9. Acid 11, $C_{23}H_{16}O_4$, m.p. 220°C (decomp.), ν_{max} 3200-2300, 1695, 1590 cm^{-1}, λ_{max}^{EtOH} 282, 293 and 312 nm (log ε 3.79, 3.84 and 3.97), was obtained by alkaline hydrolysis of the dihydro ester 10. Whereas, alkaline hydrolysis of the hydroxy ester 8 under nitrogen atmosphere, gave orange silky needles 12, $C_{22}H_{14}O_2$ m.p. 160°C (decomp.), m/e; M^+ 310, ν_{max} 1635 (weak absorption), 1600, 1580 cm^{-1}, λ_{max}^{EtOH} 242, 261, 268, 400, 423, 447 and 473 nm (log ε 4.50, 4.41, 4.36, 3.92, 4.06 4.11 and 3.89), δ_{CDCl_3} 6.04 (s. 1H), 6.60-8.05 ppm (m. 13H). The orange compound 12 was also obtained upon treatment of the red ester 9 with alkali. On catalytic reduction with platinum oxide in ethanol, 12 resulted in absorption of two moles of hydrogen to give a tetrahydro compound 13, $C_{22}H_{18}O_2$, m.p. 170°C (decomp.), m/e M^+ 314, ν_{max} 1600, 1500, 770, 760, 707 cm^{-1}, λ_{max}^{EtOH} 283 and 310 nm (log ε 3.69 and 3.70). Methylation of the hydroxy ester 8 with dimethyl sulfate and aqueous alkali in ethanol at 0°C, gave a methyl ether 14, $C_{25}H_{20}O_5$, m.p. 145-147°C, ν_{max} 1730, 1610, 1580, 760, 750, 738 cm^{-1}, λ_{max}^{EtOH} 240, 295.5, 307, 342 and 364 nm (log ε 4.23, 4.07, 3.95, 4.21 and 4.17), δ_{CDCl_3} 3.15 (s. 3H), 3.97 (s. 3H), 5.52 (s. 1H), 6.70-7.90 ppm (m. 13H). However, treatment of 8 with methyl iodide and potassium carbonate in refluxing acetone did not afford 14 but the methyl ether 4 described above. When the hydroxy ester 8 was treated with oxygen in the mixture of aqueous sodium hydroxide, tetrahydrofuran, and ethanol, the dilactone 5 was obtained.



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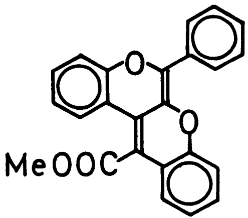

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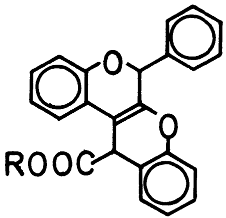
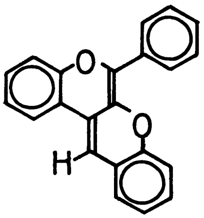


10 R=Me
11 R=H



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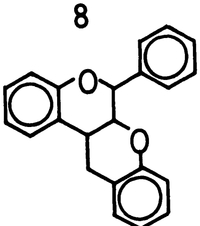

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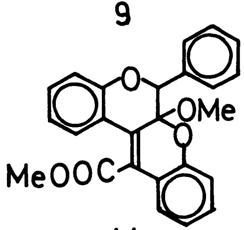

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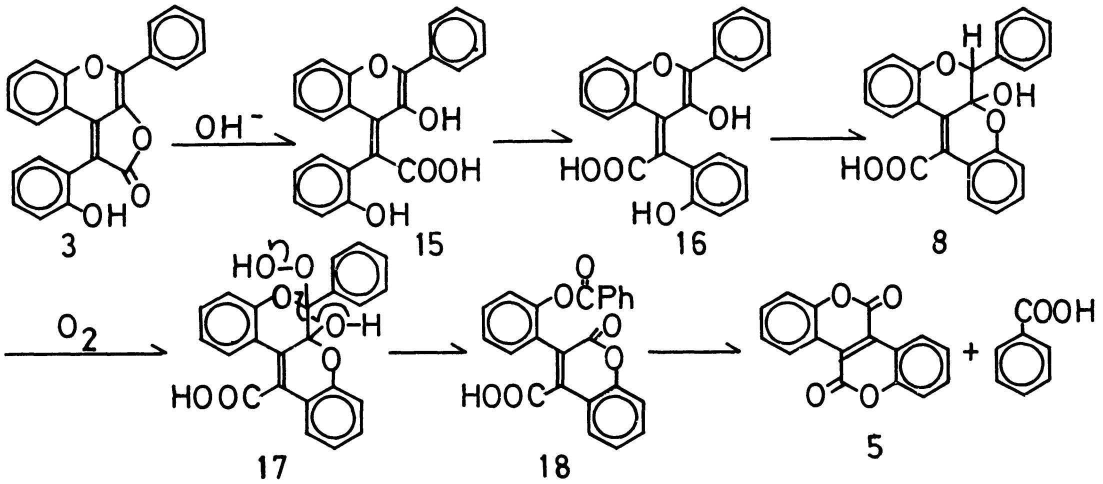
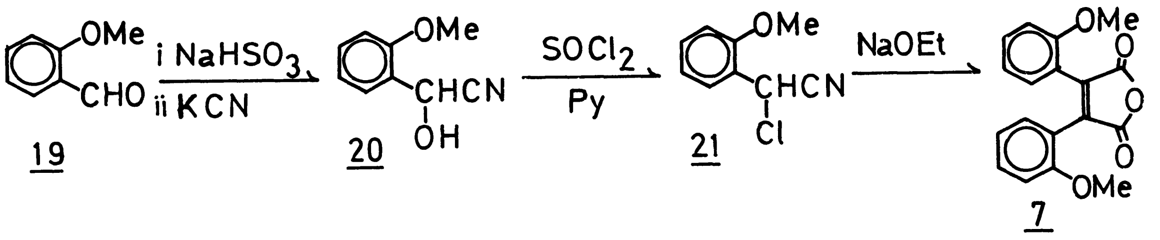
From the above evidence, it is presumed that the autoxidation of the hydroxy compound 3 to the dilactone 5 proceeded according to the mechanism as shown in the scheme 1 ; e.g. hydrolysis of lactone ring, isomerization of C-C double bond, ring closure to a hemiketal and then formation of hydroperoxide at benzylic position followed by cleavage of β-hydroperoxy hemiketal and relactonization. Of course, treatment of photoflavanonol-red with oxygen in the alkaline solution, also gave the dilactone 5.

Scheme 1



In order to confirm whether the photooxygenation occurred with singlet oxygen, we carried out the oxidation of the flavanonol-red with H_2O_2-NaOCl system.[4] On this reaction, photoflavanonol-red was expectedly obtained though low yield. Therefore, it was confirmed that photoflavanonol-red was formed by oxygenation of flavanonol-red with singlet oxygen produced by the photosensitization of molecular oxygen with flavanonol-red itself.

Scheme 2



References

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3) P. Chovin, Bull. soc. chim. France, [5] 11, 82 (1944).
4) R. W. Denny and A. Nickon, Organic Reactions, Vol. 20, 133 (1973).

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