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PHOTO-OXYGENATION OF TROPONE. A CONVENIENT SYNTHESIS OF 5-HYDROXYTROPOLONE AND TROPOLONE

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In the last year Forbes and Griffiths reported that photo-oxygenation of tropolone methyl ether gives an epidioxide.[2] We have explored independently photo-oxygenation of heptafulvenes[3] and tropones and found that they easily give epidioxides. We here report the reaction of tropone and some chemical properties of the epidioxide.

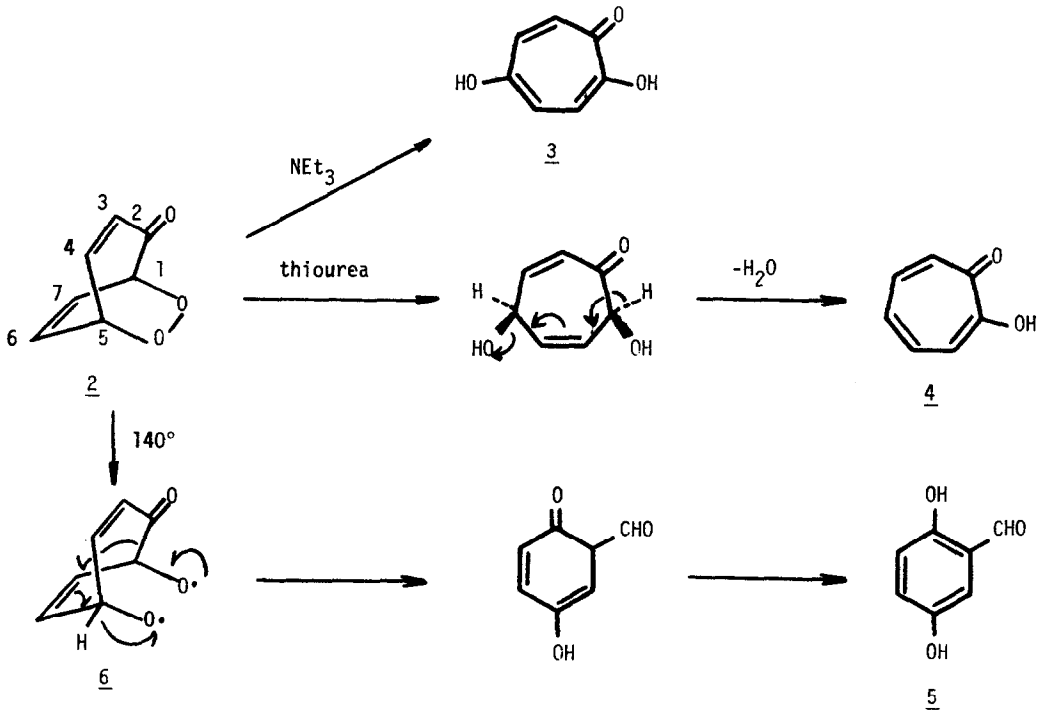
Tropone (1) absorbed one mole of oxygen when irradiated in acetone containing hematoporphyrin as sensitizer under oxygen with a 300 W tungsten lamp for 21 hrs. Evaporation of the solvent under reduced pressure below 50°C and passing through a short silica-gel column gave an epidioxide (2) in more than 90% yield as pale yellow liquid; IR: ν_{max}(liquid) 3050, 2960, 1690, 1617, 972, 945, 915, 887, 830, 748 and 670 cm^{-1}; UV: λ_{max}(iso-octane) 214 mμ (log ε 3.84), 248^{sh}(3.00), 290^{sh}(2.45). Rose Bengal also serves as sensitizer, but it is decolored during the irradiation and the yield is relatively low. The infrared and ultraviolet spectra indicate the presence of an α,β-unsaturated carbonyl group. The NMR spectrum (60 MHz, $CDCl_3$) exhibits signals at δ, 7.09 (dd, J=11.0 and 7.6 Hz, H_4), 7.03 (ddd, 8.2, 7.4 and 1.1, H_6 or H_7), 6.52 (ddd, 8.2, 7.7 and 1.1, H_6 or H_7), 5.98 (ddd, 10.8 2.0 and 1.1, H_3) and 5.23-4.85 (m, H_1 and H_5), which further confirms the structure as shown.

The epidioxide (2) is fairly stable in aprotic solvents at room temperature, but explodes above 120°C in a capillary tube.

Treatment of 2 with triethylamine in ethanol at room temperature resulted in a facile cleavage of the epidioxy linkage to give 5-hydroxytropolone (3)[4] in quantitative yield. This procedure may be the most convenient method for the synthesis of 3 so far reported.[2,4,5]

Selective reduction of 2 with thiourea[6] gave tropolone (4) in 77% yield.

On refluxing in xylene, 2 underwent a rearrangement to give 2,5-dihydroxybenzaldehyde (5) in 53% yield. Although we have now no proof for the mechanism, the reaction might be initiated from the homolysis of O-O bond to give a diradical (6) as follows.



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