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PHOTO-OXYGENATION OF 2,3-HOMOTROPONE AND SYNTHESIS OF 1,2-DIOXOCYCLOOCTA-3,5-DIENE FROM THE EPIDIOXIDE

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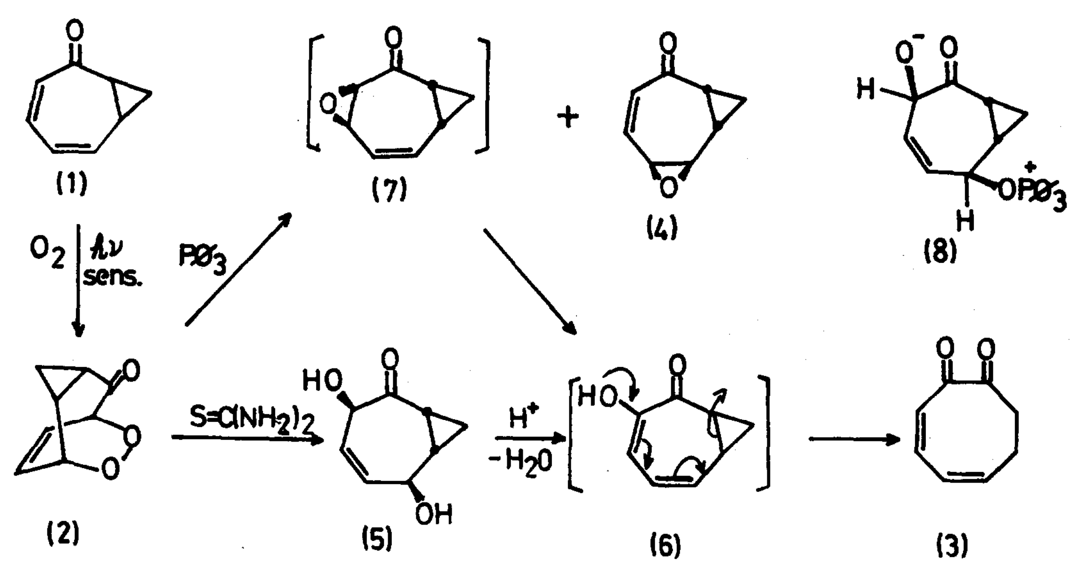
2,3-Homotropone[1] (1) readily undergoes Diels-Alder reaction with some typical dienophiles.[2] We have reported the photo-oxygenation of tropone which provides a simple way for the preparation of 5-hydroxytropolone and tropolone.[3] We now report that (1) also reacts with singlet oxygen to give the epidioxide (2) which in turn can be converted into previously unknown 1,2-dioxocycloocta-3,5-diene (3) by the intermediacy of 7-hydroxy-2,3-homotropone.

Photo-oxygenation of (1) in acetone using hematoporphyrin as a sensitizer (room temperature, a few days) gave the epidioxide (2) in 90% yield [m.p. 80-81°C; ν_{max}(KBr) 3110, 3045, 1695, 956, 920, and 705 cm^{-1}; δ (CDCl$_3$) 6.7-6.2 (m, 2H), 5.30 (m, 1H), 4.68 (m, 1H), 1.89 (m, 2H), and 1.4-0.7 ppm (m, 2H)]. Although no decisive evidence has been yet obtained, the orientation of the cyclopropyl group may be *anti* from the view-point of steric hindrance.[4]

Treatment of (2) with triphenylphosphine (1 equiv., dichloromethane, 0°C) afforded two deoxygenated products, (3) (47%) and 6-oxatricyclo[6.1.0.0^{5,7}]nonene-3-one-2 (4) (12%) [(3): ν_{max} 1720, 1655, and 1597 cm^{-1}; λ_{max}(EtOH) 215 (log ε 3.51) and 284.5 nm (3.67); δ (CCl$_4$) 6.62 (dd, J=11.8, 5.8 Hz, 1H), 6.4-5.8 (m, 3H), and 2.9-2.3 (m, 4H); (4): ν_{max} 1660, 1640, and 1595 cm^{-1}; λ_{max}(FtOH) 220 (sh, 3.66), 255 (sh, 3.24), and 290 nm (2.83); δ (CCl$_4$) 6.17 (dd, J=12.0, 4.5 Hz. 1H), 5.53 (dt, 12.0, 1.2, 1H), 3.62 (t, 4.5, 1H), 2.95 (ddd, 5.3, 4.5, 1.2, 1H), and 2.3-1.2 ppm (m, 4H)]. The relationship between the two three-membered rings of (4) may be *anti* from the standpoint of *anti* configuration of (2).

Selective reduction of the epidioxy group of (2) with thiourea (1.1 equiv., tetrahydrofuran, room temperature) gave the dihydroxyketone (5) in 96% yield [ν_{max} 3350 and 1680 cm^{-1}; δ (CDCl$_3$) 5.94 (dd, J=12.0, 1.5, 1H), 5.56 (dd, 12.0,



3.0, 1H), 4.70 (m, 2H), 4.10 (br. s, 2 OH), 2.0 (m, 2H), and 1.4 ppm (m, 2H)]. In chloroform solution at room temperature, the dihydroxyketone (5) slowly underwent dehydration and gave (3), probably catalyzed by a trace amount of hydrogen chloride present in chloroform. Accordingly, compound (3) was more conveniently obtained in 76% yield by heating to reflux of (5) in chloroform at the presence of *p*-toluenesulfonic acid for 1 hr.

The formation of (3) in both reactions can be explained by the intermediacy of 7-hydroxy-2,3-homotropone (6). In the case of deoxygenation with triphenylphosphine, (6) may be formed from 4-oxatricyclo[6.1.0.$0^{3,5}$]nonene-6-one-2 (7) by isomerization or directly from (8). Thus 7-hydroxy-2,3-homotropone (a σ-homotropolone) (6) seems to exist only as a transient species and to isomerize spontaneously to (3).

Attempts to convert (3) into the interesting but yet unknown 1,2-dioxocycloocta-3,5,7-triene are under way.

References

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4) Anti configuration was also assigned for the Diels-Alder adducts in lit. 2 on the same reason.