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THE SENSITIZED PHOTOOXIDATION OF 7,7'-BICYCLOHEPTATRIENYL: FORMATION OF DOUBLE $(4+2)\pi$ TYPE PEROXIDES TOGETHER WITH BIPHENYL AND 7-PHENYLCYCLOHEPTATRIENE

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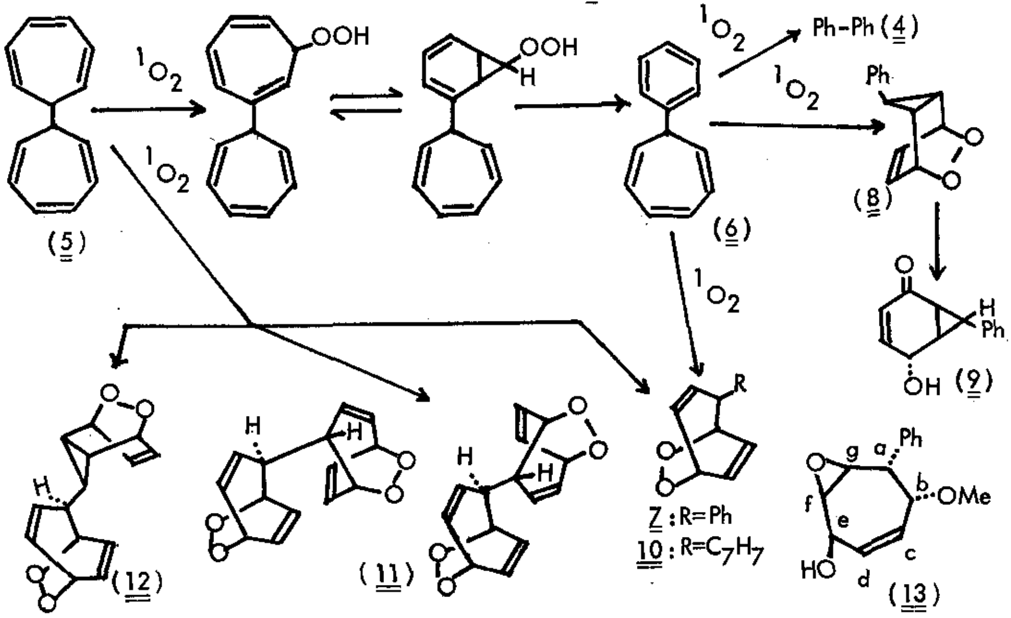
In the presence of Methylene Blue, photooxygenation of the title olefin gave several double $(4+2)\pi$ cycloadducts with oxygen. Structures of these products were deduced by analysis of the ^{1}H- and ^{13}C-NMR spectra. In addition, formation of biphenyl, 7-phenylcycloheptatriene and its oxidation products in the reaction invalidated the previously proposed mechanism for the tropone formation.

In 1957, Schenck has reported the sensitized photooxidation of cycloheptatriene (1) to give tropone (2) in a low yield, and suggested a dehydration of 7-hydroperoxycycloheptatriene (A), unidentified intermediate, for the genesis.[1] Later on, more detailed study by Kende and Chu reproduced his results and further identified other modes of the reaction by characterizing the products after catalytic reduction.[2] However, the full analysis of the products was at first performed by Kitahara *et al.*,[3] who have although obtained 2 by a sequence of transformations of the $(6+2)\pi$- and $(4+2)\pi$-adducts, the original proposal, A to 2, was overlooked without examination. Meanwhile, the hydrogen peroxide oxidation of tropylium bromide4) and ditropylium sulfate5) are known to give solely benzene (3) and biphenyl (4), therefore, an intermediacy of A for the process seems to be questionable even under the photooxygenation conditions.

When a methanol solution of 7,7′-bicycloheptatrienyl (5) was irradiated by a 500 W tungsten lamp with Methylene Blue under an oxygen atmosphere, the reaction occurred to give rather complicated products: The hydrocarbon fractions consisted of 4 (3 %) and 7-phenylcycloheptatriene (6, 5 %). Subsequently, four crystalline products, 7 (6 %), mp 115-116°C, 8 (1 %), mp 94-96°C, 9 (9 %), mp 146-148°C, and 10 (2 %), mp 174-175°C, were isolated. 7, 8 and 9 were identical with the authentic samples prepared by Kitahara et al. (lit.3b) mp 95-97°C, 92-93°C, and 145-145.5°C).6) 10 was recently obtained by the benzil-sensitized photooxidation of 5.7)

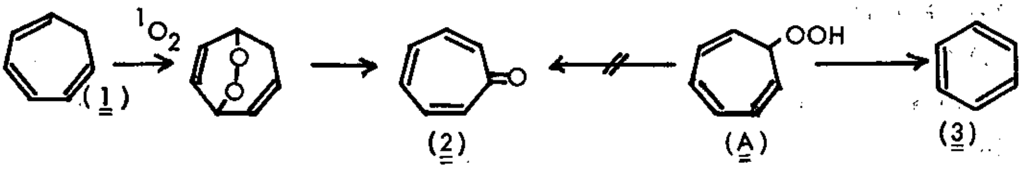


Other than the phenylated products, bis-oxygen-adducts, 11 (1 %), mp 185-186°C, and 12 (1 %), mp 149-150°C, were isolated from the next fractions. According to the ^{13}C-NMR spectrum,8) 11 [δ9): 45.3, 73.6, 79.1, 123.9, 128.8, 132.6, and 136.2 for a-isomer. 48.1, 73.4, 78.5, 124.6, 129.3, 133 4, and 135.1 for b-isomer] is a mixture of racemic and meso compounds. 12 exhibited fourteen lines of the ^{13}C-NMR [δ:

11.3, 11.4, 18.9, 47.3, 72.6_7, 72.7_4, 73.5, 78.7, 124.4, 127.8, 128.6, 133.8, and 136.1] which are indicating four carbons bearing oxygen substituents and a cyclopropane ring together with three double bonds. Assuming the direction of attack of the oxygen to be *anti* to the other cycloheptatriene group, the stereostructure of 12 can be deduced as shown in the chart. Although there is another product, 13, colorless crystals, mp 103-104°C (3 %),[10] no tropone derivative has been detcted in the reaction mixture.

An involvement of singlet oxygen in the oxygenation was secured by quenching experiments[11] and the rate enhancement in the *deuterio*-solvents.[12] Thus, an addition of diazabicyclooctane (DABCO, 3.1 molar equivalent to 5) caused a rate retardation to 12.4 %, but the yields of 6 based on the consumed 5 were same within experimental error (2.5 % with DABCO and 4 % without DABCO). In addition, the yields of 6 and 4 at the stage of 65 % conversion were comparable in both solvents, 5.5 % and 0.4 % (in methanol) and 5.5 % and 0.6 % (in methanol-d_4 where a rate enhancement for the oxygenation was 8.4 times).

Finally, benzene, 3, was indeed obtained by the singlet oxygen oxidation of 1 in 10 % together with the other products in similar yields to the recent report.[3a] Again, 2 was isolated only after the silica gel column chromatography. Therefore, tropones can not be the primary products of the reaction, and their precursors should be survived until the work up. Hydroperoxycycloheptatrienes, like A, must not be the case,[13] and the previous proposal, A to 2, is invalid.[14,15]



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6) The ^{13}C-NMR in CDCl$_3$ disclosed following figures: 6, 52.1, 73.7, 80.9, 124.8, 127.4, 128.4(2C), 128.5(2C), 129.4, 134.8, 134.9, and 136.2. 7, 15.7(2C), 24.2, 72.9(2C), 126.3, 126.4(2C), 127.6(2C), 128.4(2C), and 139.3. 8, 32.2, 32.4, 35.3, 62.3, 126.1(3C), 127.0, 128.6(2C), 138.3, 143.3, and 194.6.

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8) The ^{1}H-NMR of 11a and 11b revealed overlappings of signals. The assigned stereochemistry is based on the preferred attack of oxygen from the less hidered side, anti to the other cycloheptatriene group.

9) The NMR spectra were obtained in CDCl$_3$ solutions with the internal standard, TMS.

10) 13 is a secondary product. Its structure was deduced by measurements of NMR[δ: 3.0(Hg, m), 3.19(3H, s), 3 36(Hb, ddd, J=4, 2, 1.5 Hz), 3 62(Hf, ddd, J=4, 2, 1.5 Hz), ca. 4(He, br., overlapped), 4.04(Ha, d, J=7 Hz), 5.11(Hc, ddt, J=10.5, 4.5, 2 Hz), 5.47(Hd, ddt, J=10.5, 2, 1.5 Hz), and 7.3(5H, m)] and derivations into an acetate[δ: 2.10(3H, s), 3.08(Hg, m), 3.20(3H, s), 3.44(Hb, m), 3.56(Hf, m), 4.08 (Ha, d, J=7 Hz), 5.34(Hc, Hd, and He, m), and 7.3(5H, m)] and an unsaturated ketone[δ: 3.22(3H, s), 3.34(Hb and He, m), 3.96(Hf, ddd, J=3.5, 2, 1 Hz), 4.12(Ha, d, J=7.5 Hz), 5.90(Hd, ddd, J=10.5, 1.5, 1 Hz), 6 10(Hc, ddd, J=10.5, 4.5, 2 Hz), and 7.3(5H, m)], both colorless oils.

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13) Gas-liquid chromatographic analysis of benzenes after sodium borohydride reduction of the reaction mixture excluded their formation in the chromatography column.

14) The formation of benzaldehyde, a by product, was also explained in terms of a rearrangement of A.3a) We prefer an alternative route, recyclization of heptadienedials, cleavage products of dioxetanes, on the same ground.

15) 2 has been experimentally obtained from the $(4+2)\pi$ cycloadduct.3a)

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