CHEMISTRY LETTERS, pp. 127-130, 1978. Published by the Chemical Society of Japan

SINGLET-OXYGEN REACTIONS OF 1,4-CYCLOHEXADIENE. A SYNTHETIC APPROACH TO THE BENZENE-1,4-ENDOPEROXIDE[1)]

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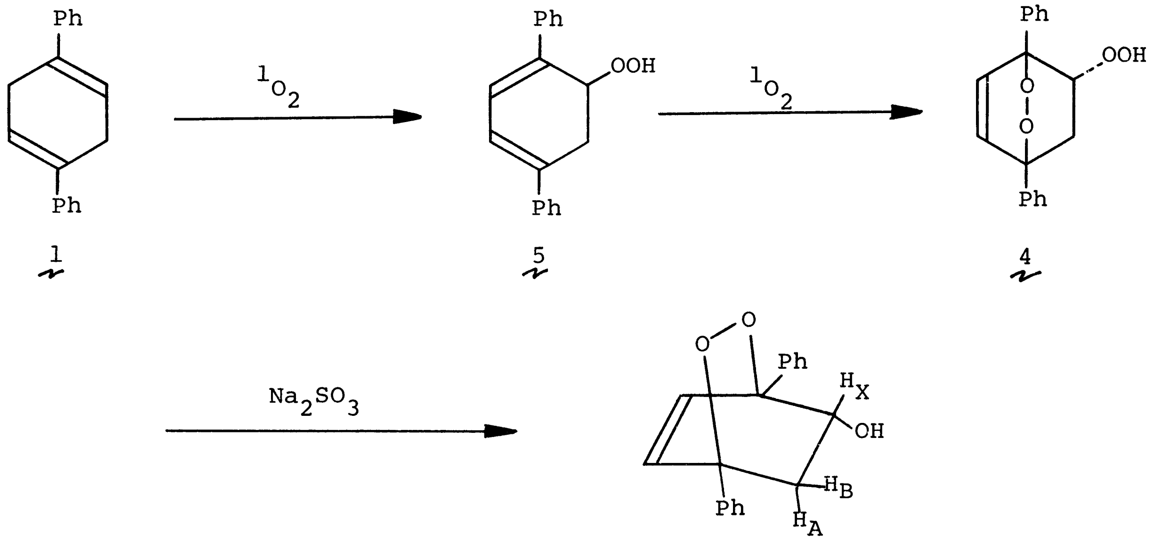
Dye-sensitized photooxygenation of 1,4-diphenyl-1,4-cyclohexadiene (1) at 0 °C followed by reduction with sodium bisulfite gave 1,4-diphenyl-7-hydroxy-5,6-dioxabicyclo[2.2.2]oct-2-ene (2). Mesylation of 2 followed by treatment with potassium t-butoxide yielded p-terphenyl, accompanied with the generation of singlet oxygen.

While the endoperoxides of polycyclic aromatic systems such as anthracenes and substituted naphthalenes[2)] resulting from the addition of singlet oxygen are well known,[3,4)] the endoperoxide of benzene derivatives has not been reported so far. We previously reported that highly electron-donor substituted benzenes undergo reaction with singlet oxygen to give products which are believed to derive from 1,4-endoperoxides.[5,6)] Recently, Schäfer-Ridder et al. have reported the first synthesis of the naphthalene-1,4-endoperoxide which readily decomposes to naphthalene and singlet oxygen with half-life of 303 min at 20 °C.[7)] We now wish to report our approach to the synthesis of the hitherto unknown benzene-1,4-endoperoxide system.

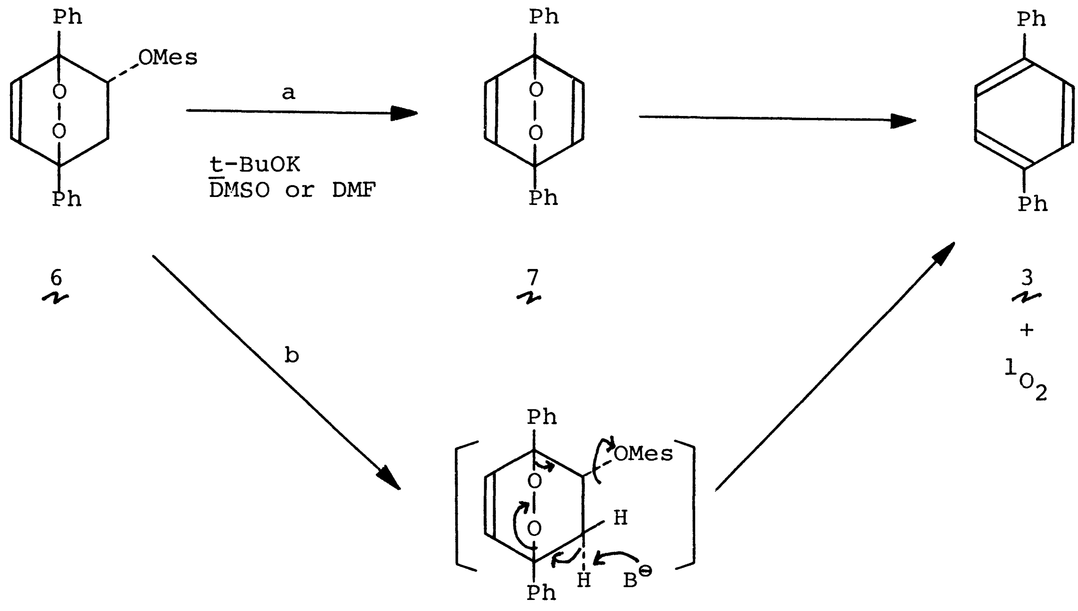
Rose bengal-sensitized photooxygenation[8)] of 1,4-diphenyl-1,4-cyclohexadiene (1)[9)] (5 mM) in $CHCl_3$-acetone (1 : 4) at 0 °C followed by treatment with aqueous sodium bisulfite gave the endoperoxide 2 (62%) and p-terphenyl (3) (10%).[11)] The structure of 2[12)] was assigned on the basis of the following spectral data: mp 130-133 °C (dec); IR (KBr) 3500, 1080 cm^{-1}, NMR ($CDCl_3$)[13)] δ 1.90 (dd, 1 H, J_{AB} = 14 Hz, J_{AX} = 2 Hz, H_A), 3.00 (dd, 1 H, J_{AB} = 14 Hz, J_{BX} = 8 Hz, H_B), 4.50 (dd, 1 H, J_{AX} = 2 Hz, J_{BX}= 8 Hz, H_X), 6.90 (d, 1 H, J = 9 Hz), 7.08 (d, 1 H, J = 9 Hz), 7.20-7.80 (m, 10 H, arom H). When the same photooxygenation was carried out at 0 °C and the reaction mixture was purified by preparative tlc, unstable hydroperoxide 4[15] was obtained in low yield. The hydroperoxide 4 was slowly decomposed on silica gel to yield a complex mixture of products including 2 and 3. The formation of 2 suggests an "ene" reaction giving 5 in the first stage, followed by 1,4-cycloaddition of a second singlet-oxygen molecule.[16]



1 5 4

2

Reaction of 2 with methanesulfonyl chloride and triethylamine in CH_2Cl_2 at 0 °C yielded the mesylate 6[12] (90%): mp 80 °C (dec), IR (KBr) 1360, 1100 cm^{-1}; NMR ($CDCl_3$) δ 2.13 (dd, 1 H, J = 14 Hz, J' = 3 Hz), 2.30 (s, 3 H), 2.94 (dd, 1 H, J = 14 Hz, J' = 8 Hz), 5.00 (dd, 1 H, J = 8 Hz, J' = 3 Hz), 6.78 (d, 1 H, J = 8 Hz), 7.00 (d, 1 H, J = 8 Hz), 7.20-7.80 (m, 10 H). Treatment of the mesylate 6 with *t*-BuOK in DMSO or in DMF at room temperature for 2 hr gave *p*-terphenyl 3 in nealy quantitative yield; no other products were detected on the tlc. When the reaction of 6 with *t*-BuOK was carried out under nitrogen atmosphere in DMF in the presence of 1,3-diphenylisobenzofuran[18] as a singlet-oxygen acceptor, *o*-dibenzoylbenzene was formed in *ca.* 20% yield (based on the reacted 6), accompanied with the formation of 3. The result suggests that 2 and singlet oxygen are formed *via* the benzene-1,4-endoperoxide 7 (path a) or directly from 6 by the elimination reaction (path b). In order to get spectroscopic evidence for the intermediacy of 7, we carried out the reaction in d_7-DMF at -5 ∿ 0 °C in a NMR cell. The NMR spectrum (-10 °C) of the mixture showed the



presence of only 3 and 6. At below -10 °C the reaction did not proceed and the mesylate 6 was remained unchanged. The results described here suggest that the benzene-1,4-endoperoxide 7, if formed, might be unstable at 0 °C to decompose to p-terphenyl and singlet oxygen.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan and the Japan Society for the Promotion of Science.

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8) Irradiation was made with a tungsten-bromine lamp through an aqueous $CuCl_2$-$CaCl_2$ filter solution.

9) Prepared by the known method.10) Pure **1** was obtained in low yield by repeated recrystallizations of the 1,4- and 1,3-cyclohexadiene mixture. For preparative purpose, a mixture (1 : 1) of the isomers was used as the starting compound.

10) J. Dale and P. O. Kristiansen, *Acta Chem. Scand.*, **25**, 359 (1971).

11) The products were isolated by thick-layer chromatography (silica gel).

12) All new compounds gave satisfactory elemental analyses and mass spectral data.

13) Downfield shift of H_B proton has also been observed in the model compound,14) whereas a strongly shielded proton is ascribable to H_A proton by inspection of the Dreiding model.

14) D. J. Coughlin and R. G. Salomon, *J. Am. Chem. Soc.*, **99**, 655 (1977).

15) Viscous oil: starch-KI test positive; NMR ($CDCl_3$) δ 2.05 (dd, 1 H, J = 14 Hz, J' = 2 Hz), 2.95 (dd, 1 H, J = 14 Hz, J' = 8 Hz), 5.00 (dd, 1 H, J = 8 Hz, J' = 2 Hz), 6.80 (d, 1 H, J = 9 Hz), 6.90 (d, 1 H, J = 9 Hz), 7.25-7.60 (m, 10 H); mass spectrum (m/e) 262 (M^+- 34), 230.

16) Analogy for this process has recently been reported in the reaction of hexamethylbenzene with singlet oxygen.17)

17) C. J. M. Van Den Heuvel, H. Steinberg, and T. J. De Boer, *Rec. Trav. Chim.*, **96**, 157 (1977).

18) A similar result was obtained with tetramethylethylene.

(Received November 9, 1977)