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THE SYNTHESIS OF THE ENDOPEROXIDE OF CYCLOOCTATETRAENE VIA PHOTOSENSITIZED SINGLET OXYGENATION

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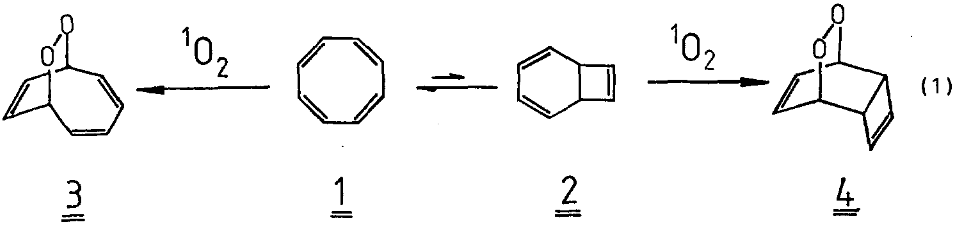
SUMMARY: 7,8-Dioxabicyclo[4.2.2.]deca-2,4,9-triene (3), the hitherto unknown endoperoxide of cyclooctatetraene, was prepared via cycloaddition of singlet oxygen and characterized by spectroscopic and chemical means.

Recently we reported[1] the synthesis of anti-7,8-dioxatricyclo[4.2.2.$0^{2,5}$]deca-3,9-diene (4), directly from the labile bicyclic valence isomer 2 of cyclooctatetraene (1) via singlet oxygenation (eq.1) at low temperature. Also a number of its chemical transformations were described[2], which demonstrated the synthetic utility of such readily accessible endoperoxides.



(1)

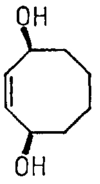
Equally useful for synthetic exploration would be the endoperoxide 3, derived from cyclooctatetraene (1), but unfortunately 1 is inert towards dyestuff-sensitized singlet oxygenation[3]. It was shown[4] that cyclooctatetraene (1) is an efficient quencher of the triplet state excited dyestuff, so that no $^1O_2$ is formed for reaction with 1. Even chemical singlet oxygenation with the endoperoxide of 1,4-dimethoxy-9,10-diphenylanthracene at elevated temperatures did not afford

3.[5] However, we now present the successful preparation of the desired endoperoxide **3** directly from cyclooctatetraene (**1**) via photooxygenation.

For this purpose it was necessary to develop a special immersion photosensitization apparatus for the efficient production of singlet oxygen. A high presssure250-W sodium vapor lamp (Osram NAV-TS 250W) was used as irradiation source, which was placed into the innermost well of the photovessel, efficiently cooled by circulating appropriate coolant (ca. -40°) through the surrounding cooling jacket. Irradiation of a magnetically stirred and externally cooled (-20°C) 0.75 *M* solution of cyclooctatetraene in acetone,containing 10^{-3} *M* hydroquinone as radical inhibitor and 10^{-4} *M* tetraphenylporphyrin (TPP) as sensitizer, continuously for 340 h (ca. 14 days) indicated 90% consumption of cyclooctatetraene by TLC on silica gel and ^{1}H-NMR. Besides undefined polymeric peroxides (CAUTION: highly explosive!), the desired endoperoxide **3** was isolated in 40% yield after fractional crystallization of the crude product, silica gel chromatography at -20°C using as eluant and repeated recrystallization from isopropyl alcohol.

Endoperoxide **3** is a thermally labile, white, crystalline solid, mp 34.5-36.0°C, which exhibits the following spectral properties: 400 MHz ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm) 4.87-4.92 ($H_{1,6}$, 2H, m), 4.99-5.03 ($H_{9,10}$, 2H, dd) and 5.03-5.19 ($H_{2,3,4,5}$, 4H, m); 100.3 MHz ^{13}C-NMR ($CDCl_3$, TMS) δ(ppm) 72.89 ($C_{1,6}$, d), 119.72 ($C_{9,10}$, d), 127.94 ($C_{3,4}$, d) and 131.57 ($C_{2,5}$, d); IR (CCl_4) ν(cm^{-1}) 3030, 2950, 2900, 1425, 1290 and 1250; satisfactory elemental composition for $C_8H_8O_2$ by combustion analysis.

Among the chemical transformations that serve as confirmation of the proposed endoperoxide structure for **3**, catalytic hydrogenation (methanol, Pd/C) gave first the *cis*-3,8-dihydroxycyclooctene **5** [6a,b], which on further hydrogenation (methanol-ethylacetate mixture, Pd/C) led to the fully saturated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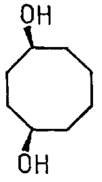
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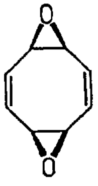
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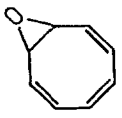
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cis-1,4-diol 6 [7], photolysis (CH_2Cl_2, 330-360 nm) afforded the diepoxide 7 [8], and deoxygenation with dimethylphosphine (CH_2Cl_2, -60°C) produced the monoepoxide 8 [9]. All these already known products were fully characterized by comparison of their physical and spectral properties with the reported ones.

On the basis of these physical, spectral and chemical data, there is no doubt that cyclooctatetraene underwent [4+2]-cycloaddition with $^1O_2$ to result in the hitherto unknown endoperoxide 3. In fact, control experiments confirmed the involvement of $^1O_2$, because in the absence of TPP as sensitizer or in the presence of DABCO as quencher[10], no endoperoxide 3 was produced. Hydroquinone was necessary as scavenger to diminish free radical autoxidation of the cyclooctatetraene, which affords the dangerous polymeric peroxide.

As to the question why previous attempts[3] to singlet oxygenate cyclooctatetraene have been unsuccessful, the present study constitutes an unequaled " tour de force" in singlet oxygenation. For example, comparative experiments revealed that our new photosensitization apparatus is at least 100-fold more efficient than previous systems. However, it still required ca. 14 days to consume ca. 0.1 mole of cyclooctatetraene, underscoring that cyclooctatetraene is indeed a reluctant substrate for photosensitized oxygenation. Yet, gram quantities of the endoperoxide 3 can now conveniently be made available for the purposes of synthetic exploration. We are confident that a number of other "reluctant" singlet oxygenation substrates will prove to be of interest under these "tour de force" conditions.

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