

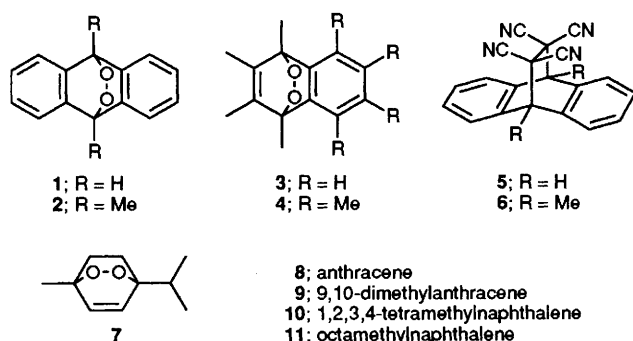
Cycloreversion of Arene Endoperoxides induced by Electron Transfer

Yasutake Takahashi, Shin-ichi Morishima, Kan Wakamatsu, Takanori Suzuki and Tsutomu Miyashi*

Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980, Japan

Cycloreversion of arene endoperoxides **1–4** can be induced by photoexcitation of their electron donor–acceptor complexes with tetracyanoethylene.

Addition of ground state triplet oxygen to 1,3-dienes is spin forbidden. However, the process can be promoted by electron transfer (ET).¹ Our own interest has been centred on the possibility that the reverse process, cycloreversion of endoperoxides, may also be induced by ET. Although the thermal and photochemical reactions of arene endoperoxides (AEs) have been extensively studied,^{2,3} little work has been done on their ET reactions.^{4a} We now report that the cycloreversion of AEs **1–4** can be induced by ET.



Photolysis of weak electron donor–acceptor (EDA) complexes is a straightforward method for ET⁵ and this technique is particularly suited to the present study since **1–4** serve as electron donors and form weak EDA complexes with tetracyanoethylene (TCNE), a typical electron acceptor. In methylene chloride the charge-transfer (CT) absorption bands of the AE–TCNE complexes appear in the visible region. The maxima were observed at 390, 412, 438, and 472 nm for **1**, **2**, **3**, and **4**, respectively. Selective irradiation (>390 nm) of only the CT absorption bands resulted in clean and efficient formation of the corresponding arenes **8–11** with evolution of oxygen, which was volumetrically determined with a gas burette to be quantitative with respect to the AEs reacted. In the cases of **1** and **2**, the resulting anthracenes were trapped as the TCNE adducts, **5** and **6**. In the reactions of **3** and **4** TCNE remained intact and could be recovered (almost) quantitatively.[†] The mass balance of the reactions is excellent and no side reaction products due to the O–O bond cleavage could be detected. The quantum yields of the photo-cycloreversion reactions at 436 nm were determined to be 0.35, 0.096, 0.12, and 0.024 for **1**, **2**, **3**, and **4**, respectively. No reaction was observed either in the dark or upon irradiation without TCNE.

These AEs, particularly **1** and **2**, underwent a clean cycloreversion by photoinduced ET whereas the thermolysis of **1** and **2** never results in the cycloreversion but leads to the O–O bond fission.^{2c,d,†} The remarkable reactivity of the AEs upon photoinduced ET stands in contrast to the fact that ascaridole **7**, a simple bicyclic endoperoxide, turned out to be stable under a similar photolysis condition though it also forms an EDA complex with TCNE and the CT absorption band appears in the visible region (λ_{max} 448 nm in methylene chloride).^{4b} Lack of reactivity of **7** upon photoinduced ET can be ascribed to the fact that the highest occupied molecular orbital (HOMO) of **7** consists of an antibonding combination of the oxygen lone pairs (π_{OO}).⁶ ET from such an antibonding HOMO would hardly be advantageous for the C–O or O–O

bond cleavage. In fact, **7** has been successfully obtained by ET-catalysed oxygenation of α -terpinene.^{1c}

On the other hand, owing to the presence of the benzene ring(s), AEs **1–4** possess additional high-lying MOs, which are close to or higher in energy than π_{OO} . In the case of **4**, for example, two important MOs, ψ_A and ψ_B , may result from a fragment interaction between the benzene ring and the double bond as qualitatively illustrated in Fig. 1(a). We have successfully isolated the **4**–TCNE complex as single crystals, suitable for X-ray crystallography.[§] The face-to-face overlapping in the CT crystals [Fig. 1(b)] is ideally suited for orbital interactions between the lowest unoccupied (LU) MO of TCNE and both ψ_A and ψ_B . Photoinduced ET from ψ_A and ψ_B would result in the corresponding singly occupied (SO) MOs. Interaction between the resulting SOMOs and the C–O σ -bonds would cause a decrease in the strength of the C–O σ -bonds and eventually lead to the extrusion of molecular oxygen.

It is interesting to examine the spin multiplicity of the evolved oxygen for the ET induced cycloreversion. If singlet oxygen ($^1\text{O}_2$) is formed, it can be trapped by a suitable trapping reagent such as tetramethylethylene (TME), which is known as a good $^1\text{O}_2$ acceptor and reacts with $^1\text{O}_2$ to give an ene-reaction product ($k = 2.4 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$).⁷ Thus, analogous photolyses of the EDA complexes of **1–4** were examined in the presence of 10 equiv. of TME, which showed that the yields of $^1\text{O}_2$ were 25, 18, 70 and ca. 0% at 30–40% conversion bases for **1**, **2**, **3**, and **4**, respectively.[¶]

Certain AEs are known to undergo thermal cycloreversion with evolution of varying yields of $^1\text{O}_2$.^{2a,b} Two mechanisms have been postulated: a concerted mechanism, which leads to quantitative yields of $^1\text{O}_2$ and a diradical mechanism, which leads to relatively low yields of $^1\text{O}_2$.^{2a} The above observations suggest that concerted loss of $^1\text{O}_2$ is unlikely. Photoexcitation of an AE–TCNE complex generates an ion radical pair [$\text{AE}^{\cdot+}$, $\text{TCNE}^{\cdot-}$] in its singlet state. Although production of $^1\text{O}_2$ and an arene–TCNE ion pair [$\text{Arene}^{\cdot+}$, $\text{TCNE}^{\cdot-}$] is spin allowed, the observed $^1\text{O}_2$ yields are not high enough to support this. The process is energetically unfavourable since $^1\text{O}_2$ is energetically higher than $^3\text{O}_2$ by 0.98 eV and the formation of the resulting ion pairs [$\text{Arene}^{\cdot+}$, $\text{TCNE}^{\cdot-}$] requires extra ion pair energy of ca. 0.65–1.12 eV.^{||} An energetically more economical pathway is to involve a diradical intermediate **12**, which can be produced by an initial cleavage of one of the two C–O

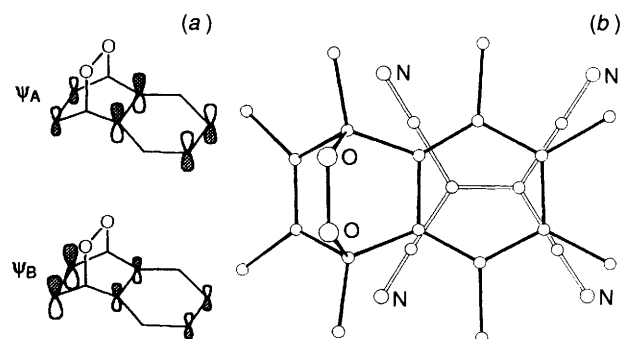
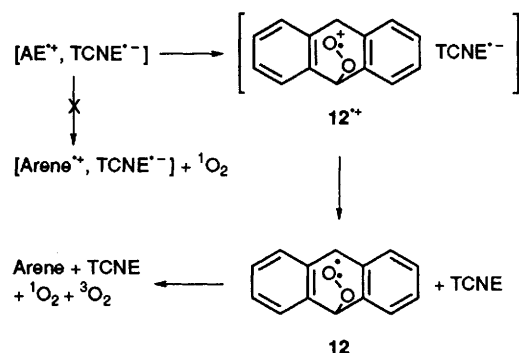


Fig. 1 (a) Qualitative illustration of two high-lying MOs of **4**. (b) Face to face molecular overlapping in the **4**–TCNE complex. The distance between TCNE and the benzene ring is 3.40 Å.



bonds of AE^{•+} in the photogenerated ion radical pair [AE^{•+}, TCNE^{•-}] followed by back ET of the resulting pair [12^{•+}, TCNE^{•-}]. Intersystem crossing in the diradical state can explain the formation of ³O₂ concomitant with ¹O₂.

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Footnotes

† Typically, an 8 cm³ methylene chloride solution of AE (0.200 mmol) and TCNE (0.200 mmol) was irradiated for 30 min by using a 500 W Xe-Hg lamp equipped with an aqueous CuSO₄ solution filter and a glass cut-off filter (>390 nm).

‡ Direct photolyses of 1 and 2 at longer wavelengths result in the O–O bond fission exclusively.^{3a} The cycloreversions may occur in competition with the O–O bond fission when photolyzed at shorter wavelengths.^{3b}

§ Crystal data: C₂₄H₂₄N₄O₂, *M*_w 400.48, monoclinic, *P*2₁/*a*, *a* = 16.679(2), *b* = 13.923(2), *c* = 19.529(2) Å, β = 107.48(1)°, *V* = 4325.6(9) Å³, *Z* = 8, and *D*_c = 1.230 g cm⁻³. No absorption correction was applied (μ_{CuKα} = 6.076 cm⁻¹). The final *R* value is 10.81% for 1910 reflections with |*F*_o| > 3σ|*F*_o| (No. of parameters 734). The

difference Fourier synthesis after the refinement gave the largest residual electron density of 0.39 e Å⁻³. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ Ten equivalent of TME is sufficient to trap ¹O₂ at low conversions. The resulting arenes 8, 9, 10 and 11 react with ¹O₂ with rate constant of 1.5 × 10⁶, 5.8 × 10⁷, 3.6 × 10⁶ and 3.1 × 10⁷ mol⁻¹ dm³ s⁻¹, respectively (CH₂Cl₂).

|| Ion pair energy can be calculated from the difference between *E*_{red} of TCNE (+0.22 V vs. SCE) and *E*_{ox} of the product arenes (+1.09, +0.87, +1.34 and +0.94 V vs. SCE for 8, 9, 10 and 11, respectively).

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