Substituent Effect on Regioselectivity in Oxygenation of Multisubstituted Acenes

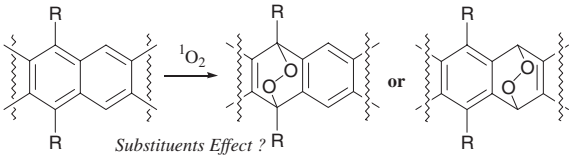
Xin Zhou, Masanori Kitamura, Baojian Shen,† Kiyohiko Nakajima,†† and Tamotsu Takahashi*
Catalysis Research Center, and Graduate School of Pharmaceutical Sciences, Hokkaido University, and SORST, Japan Science and Technology Corporation(JST), Sapporo 001-0021
†*Department of Petrochemical Engineering, Petroleum University, Beijing 102200, P. R. China*
††*Aichi University of Education, Igaya, Kariya 448-8542*

(Received January 5, 2004; CL-040009)

Reaction of substituted acenes such as anthracene, naphthacene, and pentacene derivatives with O_2 was dependent on the substituents and their positions. The orientation is in contrast to Diels–Alder reaction with DDQ in the case of naphthacene and pentacene derivatives. 1,2,3,4,5,6,7,8-Octamethylanthracene reacted with O_2 to afford a doubly oxygenated compound (diendoperoxide) at both end rings.

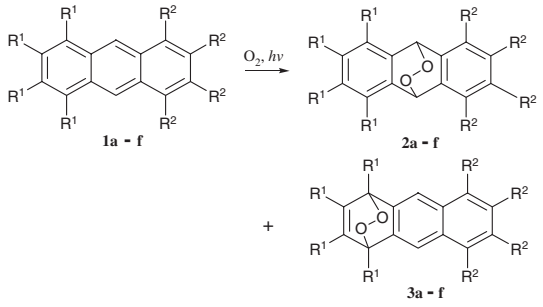
Reaction of acenes with oxygen is known to give oxygenated products, endoperoxides,[1] which have their potentials in photobiology[2] and material science.[3] However, the regioselectivity of the reaction of substituted acenes has not been well studied yet.

As shown in Scheme 1, there are two possible modes for the reaction of multisubstituted acenes with oxygen. The first mode is the reaction of oxygen at substituted carbons. And the second is the reaction at the nonsubstituted carbons.



Scheme 1.

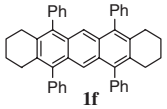
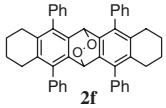
It is well known that 9,10-dialkylsubstituted anthracenes react with oxygen at the substituted carbons in the center ring.[4,5] It has been reported that when substituents were in the terminal ring, in some cases oxygen reacted with the terminal ring.[4–6] Recently we have reported the preparative method of multisubstituted acenes such as anthracenes, naphthacenes, and pentacenes.[7–10] During the course of our study, we found that the regioselectivity of the reaction of substituted acenes with oxygen was dependent on the substituents. In this paper we would like to report the substituent effect on the regioselectivity.



Scheme 2.

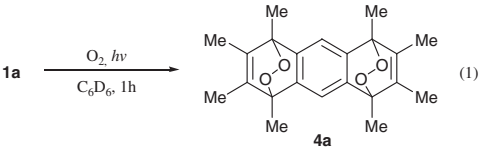
When anthracenes **1** reacted smoothly with oxygen under irradiation of 365-nm UV light, 9,10-endoperoxide **2** and 1,4-endoperoxide **3** were formed in different ratios. (Scheme 2). The result is summarized in Table 1. This reaction was very clean. In most cases, **2** was the major product. One of the structures, **2c** was determined by X-ray analysis (Figure 1).

Table 1. Photooxygenation of anthracenes **1a–f**[a]

Entry	Anthracene	R^1	R^2	NMR Yields/% Product **2**		Product **3**	
1	**1a**	Me	Me	**2a**	<5	**3a**	81[b]
2	**1b**	Et	Et	**2b**	52	**3b**	44
3	**1c**	Pr	Pr	**2c**	61	**3c**	32
4	**1d**	Bu	Bu	**2d**	57	**3d**	38
5	**1e**	Et	Ph	**2e**	53	**3e**	40
6	 **1f**			 **2f**	99	**3f**	0

[a]Anthracene 0.1–0.2 mmol, benzene-d_6 5 mL room temperature. Irradiation with a UV lamp (365 nm) for 1 h. [b]Irradiated for 15 min.

It is notable that octamethylanthracene **1a** afforded 1,4-endoperoxide **3a** in high yield with very high selectivity within 15 minutes similar to Rigauly's report (Entry 1).[6] Among **1a–d**, only **1a** gave **3** as a major product. The other **1b–d** afforded a mixture of **2** and **3** with the similar ratio. The reason is that all Me groups are on the same plane of the aromatic ring. On the other hand, the second carbons of Et, Pr, and Bu groups attached to the ring are bent to protect the ring from the reaction. This prompted us to try the further reaction of the other Me substituted terminal ring of **3a**. Surprisingly, prolongation of the irradiation time of **1a** under the same conditions produced a doubly oxygenated product **4a** (diendoperoxide) of the both terminal rings as a mixture of two isolable isomers (Eq 1).[11] The ratio of the two isomers was about 1:1.



(1)

This novel compound **4a** was characterized by NMR analysis.[12] The ^1H NMR spectra showed that characteristic protons in the aromatic ring appeared at 7.13 ppm in one isomer and at 7.15 ppm in the other isomer. Its ^{13}C NMR spectra showed only 6 carbons. A quarternary carbon signal was shown at 81.02 and

80.69 ppm, respectively. The two isomers can be considered as the stereoisomers due to the relation of two endoperoxide moieties such as *syn* and *anti*, but unfortunately, attempt of crystallization of **4a** for X-ray analysis was not successful. Although we must await further investigation for full characterization of the structure of **4a**, this is the first example of the doubly oxygenated product (diendoperoxide) at both terminal rings of anthracene derivatives.

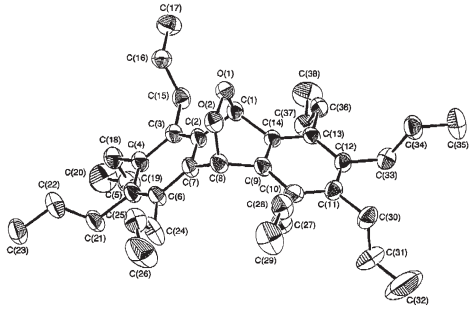
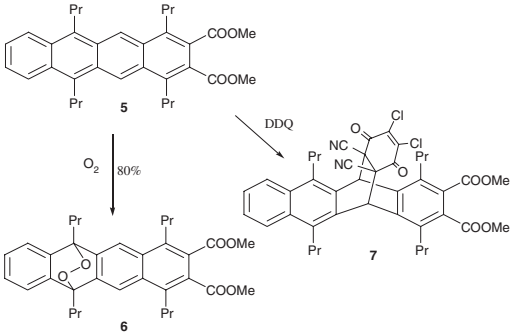


Figure 1. ORTEP drawing of **2c**.

When unsymmetrical anthracene with ethyl groups and phenyl groups **1e** was used, oxygen reacted with only the ethyl-substituted terminal ring affording **3e** selectively. The formation of 1,4-endoperoxide with oxygen at the phenyl-substituted terminal ring was not observed (Entry 5). Introduction of phenyl groups into both terminal rings such as **1f** led to the selective reaction at the center ring. 9,10-Endoperoxide **2f** was the sole product (Entry 6).

Autooxidation of substituted naphthacene **5** gave a main product **6** in 80% yield without any irradiation (Scheme 4). The structure was determined by X-ray analysis (Figure 2) It shows that endoperoxide was selectively formed at the disubstituted carbons in the internal ring. It is interesting to compare the reaction with Diels–Alder reaction of **5**. The reaction of **5** with DDQ proceeded selectively at the nonsubstituted ring carbons giving **7** as shown in Scheme 3. Steric factor has the responsibility for the selectivity at the nonsubstituted ring, although the stereochemistry of **7** is not clear yet.



Scheme 3.

Similarly, autooxidation of pentacene **8** gave a single product **9** in a quantitative yield. Cycloaddition of O_2 occurred regioselectively at the disubstituted carbon in the internal ring,[13] not at the nonsubstituted rings.[14] In contrast, addition of DDQ to **8** led to adduct **10** in 89% NMR yields (Scheme 4), accompanied with small amount of unidentified compounds. The adduct **10** was characterized by X-ray analysis.

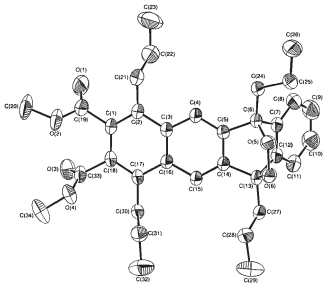
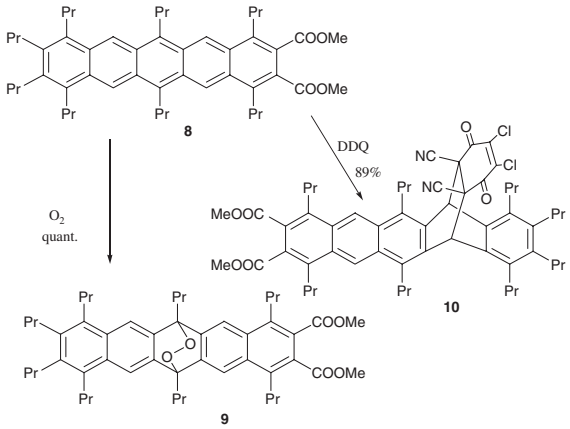


Figure 2. ORTEP drawing of **6**.



Scheme 4.

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12 **4a**; isomer A: ^{1}H NMR($CDCl_3$, Me_4Si): δ1.81(s, 24H), 7.13 (s, 2H), ^{13}C NMR ($CDCl_3$, Me_4Si): δ 12.39, 14.66, 81.02, 112.29, 138.16, 140.56. isomer B: ^{1}H NMR($CDCl_3$, Me_4Si): δ1.80 (s, 12H), 1.82 (s, 12H), 7.15 (s, 2H), ^{13}C NMR ($CDCl_3$, Me_4Si): δ 12.45, 14.62, 80.69, 112.38, 138.39, 140.56; HRMS: Calcd for $C_{22}H_{26}O_4$ 354.1831, Found 354.1821. Dec. $>$ 240 °C.
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Published on the web (Advance View) March 6, 2004; DOI 10.1246/cl.2004.410