

Photocatalytic Formation of Dimethyllepidoptere from 9,10-Dimethylantracene via Electron-Transfer Oxidation

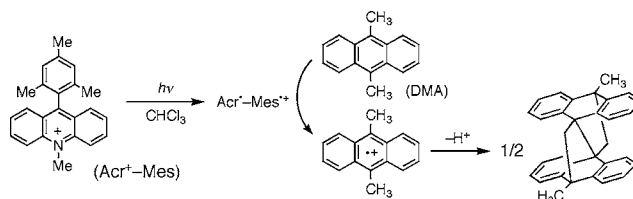
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ABSTRACT



Photocatalytic carbon–carbon bond formation of 9,10-dimethylantracene (DMA) in chloroform occurs efficiently via the electron-transfer oxidation of DMA with the photoinduced electron-transfer state of 9-mesityl-10-methylacridinium ion (Acr^+-Mes), followed by deprotonation from the methyl group of DMA radical cation and the radical coupling reaction between anthracenylmethyl radicals to produce dimethyllepidoptere.

The photochemical carbon–carbon bond formation of aromatic compounds has been extensively investigated not only for synthetic exploitation but also for basic understanding of the photochemical process.^{1–4} The mechanistic relevance of the transient species has not been firmly established in most studies, because the photoexcitation of one of the reactants leads to its excited (singlet or triplet) state, which is known to be quenched via a variety of pathways, including not only energy transfer and electron transfer but also bond formation and bond cleavage to produce a variety of reactive intermediates.^{5–9} For example, an anthracene derivative mainly gives a [4 + 4] dimer through the singlet excimer intermediate.^{4,10,11} The synthesis of another type of the anthracene dimer such

as lepidoptere (5,6,11,12-tetrahydro-4b,12[1',2'],6,10b[1'',2'']-dibenzochrysenes) has been prepared by intramolecular Diels–Alder reaction of 9-anthrylmethyl *a,p*-

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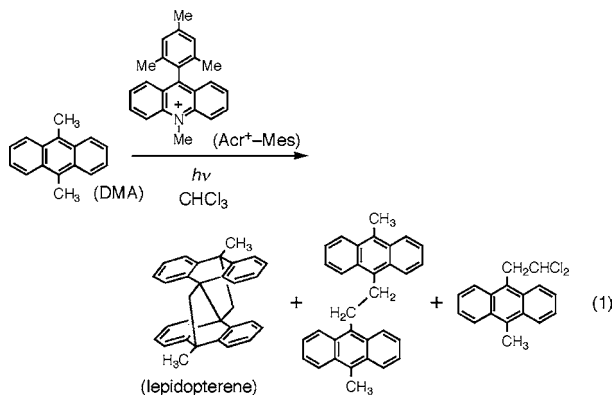
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dimer,^{10,12} dehalogenation of 9-chloromethylanthracene,¹³ oxidation of 9-methylanthracene with copper(II)/peroxydisulphate,¹⁴ photolysis of 9-(*N,N*-dimethylamino)anthracene,¹⁵ 9-(phenoxy)methylanthracene,¹⁶ and 9-anthracenylmethylsulfides and selenides.¹⁷ However, there is no report for the one-pot synthesis of the lepidoptere from the corresponding anthracene.

We report herein the synthesis of the lepidoptere from 9-methylanthracene derivatives by using the photogenerated electron-transfer state of 9-mesityl-10-methylacridinium perchlorate ([Acr⁺-Mes]ClO₄⁻).^{18,19} The photoexcitation of Acr⁺-Mes results in ultrafast intramolecular electron transfer from the Mes moiety to the singlet excited state of the Acr⁺ moiety to generate the electron-transfer (ET) state (Acr^{•+}-Mes⁺), which has an extremely long lifetime (e.g., 2 h at 203 K) and a high energy (2.37 eV).¹⁸ The ET state (Acr^{•+}-Mes⁺) has both the high oxidizing ability of the Mes⁺ moiety and the high reducing ability of the Acr^{•+} moiety.^{18,19} The photocatalytic mechanism can be firmly established by detecting radical intermediates involved in the photocatalytic cycloaddition of 9,10-dimethylanthracene.

Visible light irradiation ($\lambda = 430$ nm) of the absorption band of Acr⁺-Mes (5.0×10^{-4} M) in a deaerated chloroform (CDCl₃) solution containing 9,10-dimethylanthracene (DMA; 1.5×10^{-3} M) results in formation of dimethyllepidoptere, 1,2-bis(9-anthracenyl)ethane and 9-(β,β -dichloroethyl)-10-methylanthracene (eq 1). The photoirradiation time profiles



are shown in Figure 1. The product yields were determined as 29% and 12% for dimethyllepidoptere and 1,2-bis(9-anthracenyl)ethane, respectively, and a trace of 9-(β,β -dichloroethyl)-10-methylanthracene, after 2 h irradiation with monochromatized light at 430 nm; 53% of the photocatalyst

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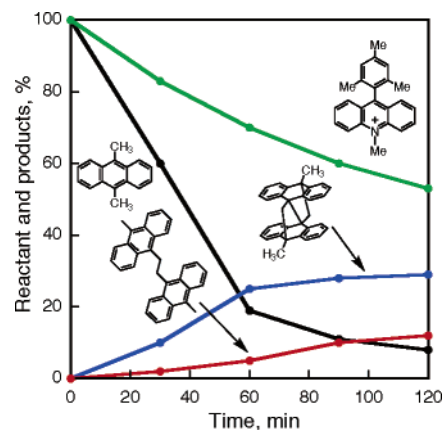


Figure 1. Irradiation time profiles of the Acr⁺-Mes-catalyzed photochemical reaction of DMA (1.5×10^{-3} M) in deaerated chloroform (0.6 mL) at 298 K; [Acr⁺-Mes] = 5.0×10^{-4} M.

still remained after 2 h of irradiation when the substrate (3 equiv) mostly reacted (Figure 1). This demonstrates efficient recycling of Acr⁺-Mes in the photocatalytic reaction. Dimethyllepidoptere was characterized by the ¹H NMR, ¹³C NMR, and EI-MS spectroscopies (see Supporting Information, S1–S3).²⁰

The photocatalytic cycloaddition of DMA in a preparative scale (60 mg, 2.9×10^{-4} mol) with Acr⁺-Mes (12 mg, 2.9×10^{-5} mol) in chloroform (10 mL) was also performed to isolate dimethyllepidoptere (12% yield) after 4 h of photoirradiation at 298 K.

Recrystallization from dichloromethane/hexane (1:1 v/v) gave pale yellow crystals of lepidoptere suitable for X-ray crystallography. An ORTEP drawing of its crystal structure is shown in Figure 2.²¹ In the crystal structure, the bond length of the newly formed C–C bond (C6–C6') is 1.629-

(19) For the C–O bond formation of anthracene radical cation with O₂^{•-} to form the [4 + 2]cycloadduct, see: (a) Kotani, H.; Ohkubo, K.; Fukuzumi, S. *J. Am. Chem. Soc.* **2004**, *126*, 15999. (b) Ohkubo, K.; Nanjo, T.; Fukuzumi, S. *Catal. Today* **2006**, *117*, 356. (c) Ohkubo, K.; Nanjo, T.; Fukuzumi, S. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1489.

(20) Typically, a chloroform solution (10 mL) containing Acr⁺-Mes (12 mg, 2.9×10^{-5} mol) and DMA (60 mg, 2.9×10^{-4} mol) in a Schlenk flask with a rubber septum was degassed by freeze-pump-thaw cycle three times and flushed with argon gas. The solution was then irradiated with a 500 W xenon lamp (Ushio Optical ModelX SX-UID 500XAMQ) through a color filter glass (Asahi Techno Glass Y43) transmitting $\lambda > 430$ nm at 298 K. After 4 h photoirradiation, dimethyllepidoptere was isolated by silica gel column chromatography (hexane/toluene 1/1, v/v) as pale yellow solid (12% yield). Dimethyllepidoptere: Anal. Calcd for C₃₂H₂₆·0.8(H₂O) C, 90.44; H, 6.55; found C, 90.59; H, 6.32. ¹H NMR (300 MHz, CDCl₃) δ 7.33 (d, *J* = 7.5 Hz, 4H), 7.02 (t, *J* = 7.5 Hz, 4H), 6.80 (t, *J* = 7.5 Hz, 4H), 6.72 (d, *J* = 7.5 Hz, 4H), 2.71 (s, 4H), 2.22 (s, 6H). ¹³C NMR (300 MHz, CDCl₃) δ 145.3, 143.8, 125.1, 124.9, 122.3, 120.4, 54.4, 42.0, 36.5, 19.0. EI-MS for C₃₂H₂₆ calcd 410.2, found 410.0. 1,2-Bis(9-anthracenyl)ethane: ¹H NMR (CDCl₃) δ 4.08 (s, 4H) 3.15 (s, 6H). (β,β -Dichloroethyl)-10-methylanthracene: MALDI-TOF-MS for C₁₇H₁₄Cl₂ calcd 288.1, found 288.4.

(21) A single crystal of dimethyllepidoptere was obtained by recrystallization from CH₂Cl₂/hexane. X-ray data for lepidoptere: monoclinic, *P*2₁/*c* (No. 14), *a* = 9.544(2) Å, *b* = 11.546(3) Å, *c* = 10.453(3) Å, β = 107.8075(9)°, *V* = 1096.6(5) Å³, *T* = 123(2) K, *Z* = 2, μ (Mo K α) = 0.070 cm⁻¹, *R*1 = 0.040 (*I* > 2 σ (*I*)), *R*w = 0.105 (all data), GOF = 1.121. For details, see Supporting Information (CIF file). A similar crystal structure has been reported briefly: Liu, Q.-X.; Song, H.-B.; Xu, F.-B.; Li, Q.-S.; Zeng, X.-S.; Leng, X.-B.; Zhang, Z.-Z. *J. Chem. Res., Synop.* **2003**, 445.

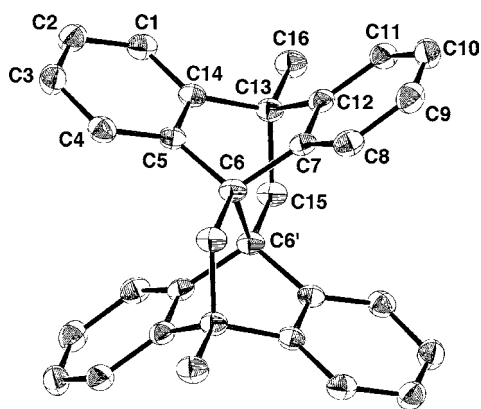


Figure 2. ORTEP drawing of dimethyllepidoptereine produced in the Acr^+ -Mes-catalyzed photochemical reaction of DMA with 50% probability thermal ellipsoids.

(2) Å, which is much longer than normal C–C single bonds, indicating severe distortion of this compound.

The quantum yields (Φ) of the photochemical reaction were determined from decay of the absorbance due to DMA ($\lambda_{\text{max}} = 402 \text{ nm}$) under irradiation of monochromatized light of $\lambda = 430 \text{ nm}$. The Φ value increases with an increase in concentration of DMA to approach a limiting value (Φ_{∞}) in accordance with eq 2

$$\Phi = \Phi_{\infty} K[\text{DMA}] / (1 + K[\text{DMA}]) \quad (2)$$

as shown in Figure 3.²² From the fitted curve in Figure 3, the Φ_{∞} value is determined as 22% in CHCl_3 . The Φ_{∞} value

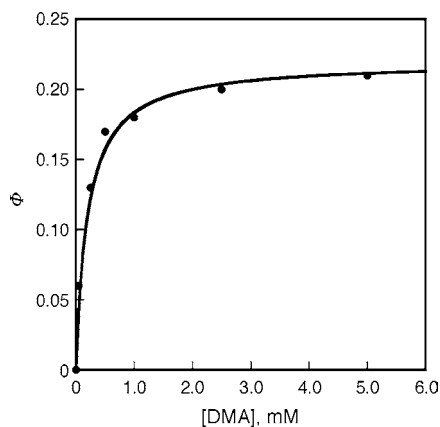


Figure 3. Dependence of the quantum yield (Φ) on concentration of DMA for the Acr^+ -Mes-catalyzed photochemical reaction of DMA in deaerated CHCl_3 at 298 K. The curve represents the best fit to eq 2 using $\Phi_{\infty} = 0.22$ and $K = 5000 \text{ M}^{-1}$; $[\text{Acr}^+ - \text{Mes}] = 5.0 \times 10^{-5} \text{ M}$.

of 9-methylanthracene was also determined to be 12% as shown in Table 1, together with the product yields of the lepidoptereine. No photodimerization has occurred in the case

Table 1. Limiting Quantum Yields (Φ_{∞}), Product Yields of Lepidoptereine, and One-Electron Oxidation Potentials of Anthracene Derivatives (E_{ox} vs SCE) in Chloroform

substrate	Φ_{∞}	yield, ^a %	E_{ox} , V
9,10-dimethylanthracene	0.22	29	1.09
9-methylanthracene	0.12	30	1.13
9,10-diethylanthracene	0	0	1.17
anthracene	0	0	1.25

^a Obtained after 2.0 h photoirradiation.

of unsubstituted anthracene or 9,10-diethylanthracene under the same experimental conditions as employed for DMA.

Nanosecond laser excitation at 430 nm of a deaerated CHCl_3 solution of $\text{Acr}^+ - \text{Mes}$ results in formation of the ET state ($\text{Acr}^* - \text{Mes}^+$) via photoinduced electron transfer from the Mes moiety to the singlet excited state of the Acr^+ moiety as shown in Figure 4a (closed circles). Since the one-electron

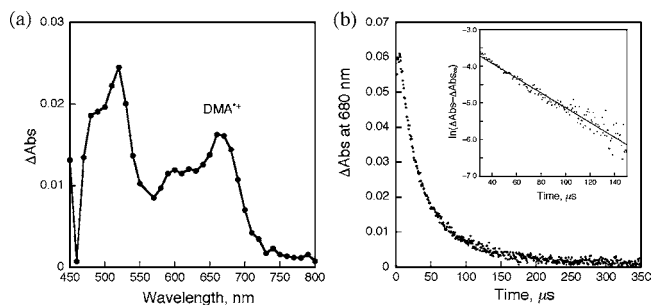


Figure 4. (a) Transient absorption spectra observed in photoinduced electron-transfer oxidation of DMA ($1.0 \times 10^{-3} \text{ M}$) with $\text{Acr}^+ - \text{Mes}$ ($1.0 \times 10^{-4} \text{ M}$) taken at $0.9 \mu\text{s}$ after laser excitation at 430 nm in deaerated CHCl_3 at 298 K. (b) Decay time profile at 680 nm. Inset: first-order plot.

reduction potential of $\text{Acr}^* - \text{Mes}^+$ ($E_{\text{red}} = 1.88 \text{ V vs SCE}$)¹⁸ is more positive than the one-electron oxidation potential of DMA ($E_{\text{ox}} = 1.09 \text{ V vs SCE in CHCl}_3$),²³ electron transfer from DMA to the Mes^+ moiety in $\text{Acr}^* - \text{Mes}^+$ is energetically feasible. Thus, the addition of DMA to a CHCl_3 solution of $\text{Acr}^+ - \text{Mes}$ and the laser photoirradiation results in formation of DMA^+ ($\lambda_{\text{max}} = 680 \text{ nm}$, $\epsilon = 6800 \text{ M}^{-1} \text{ cm}^{-1}$),²⁴ as shown in Figure 4a. On the other hand, the decay time profile of the transient absorption due to Acr^* moiety of $\text{Acr}^* - \text{Mes}^+$ ($\lambda_{\text{max}} = 520 \text{ nm}$) in the absence of DMA in

(22) A standard actinometer (potassium ferrioxalate) was used for the quantum yield determination of the photocatalytic reaction of anthracene with $\text{Acr}^+ - \text{Mes}$.

(23) The electrochemical measurements were performed on a BAS 630B electrochemical analyzer in deaerated CHCl_3 containing $0.20 \text{ M Bu}_4\text{NClO}_4$ as a supporting electrolyte at 298 K. The one-electron oxidation potentials of anthracene derivatives were determined by fast-scanning cyclic voltammetry using microelectrode (BAS; i.d. = $100 \mu\text{m}$) with 100 V s^{-1} of sweep rate.

(24) Fukuzumi, S.; Nakanishi, I.; Tanaka, K. *J. Phys. Chem. A* **1999**, *103*, 11212.

CHCl₃ obeyed first-order kinetics. The decay is faster than that in acetonitrile (see Supporting Information, S4).²⁵ Thus, electron-transfer reduction from the Acr[•] moiety to CHCl₃ takes place efficiently. The second-order rate constant for electron transfer from the Acr[•] moiety to CHCl₃ was determined to be $2.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$.

The decay time profile of DMA^{•+} obeyed first-order kinetics, which is independent of laser power intensity (5–13 mJ/pulse). The decay rate constant of DMA^{•+} was determined as $2.0 \times 10^4 \text{ s}^{-1}$. When DMA is replaced with anthracene (An), the formation of An^{•+} was also observed at 720 nm. However, the decay time profile obeyed second-order rate kinetics. The second-order rate constant was determined as $1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, which is close to the diffusion-limited value in CHCl₃ ($1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).²⁶ Thus, the second-order decay of An^{•+} is caused by bimolecular back electron transfer from Acr[•]–Mes to An^{•+}.

On the other hand, the first-order decay of DMA^{•+} is caused by the deprotonation of the methyl group of DMA^{•+}, because the methyl group of DMA^{•+} is known to be readily deprotonated to give 9-methylanthrylmethyl radical [(DMA-H)[•]] (Scheme 1).^{27,28} The dimerization of (DMA-H)[•] yields

by dissociative electron transfer to CHCl₃ to produce CHCl₂[•] and Cl⁻. The CHCl₂[•] radicals dimerize to yield 1,1,2,2-tetrachloroethane (CHCl₂CHCl₂). This was detected by GC–MS, and the yield was 20% based on the formation of dimethyllepidoptere. The radical coupling between (DMA-H)[•] readily deprotonated to give 9-methylanthrylmethyl radical [(DMA-H)[•]] (Scheme 1).³¹ The radical coupling of (DMA-H)[•] with CHCl₂[•] affords 9-(β,β-dichloroethyl)-10-methylanthracene.³²

The deprotonation from the methyl group of DMA^{•+} is the key step for formation of dimethyllepidoptere in Scheme 1. In the case of unsubstituted anthracene, there is no methyl group to be deprotonated in the radical cation. In the case of 9,10-diethylantracene, the deprotonation from the ethyl group in the radical cation may be too slow to compete with the back electron transfer. Thus, in neither case has photodimerization occurred (vide supra).

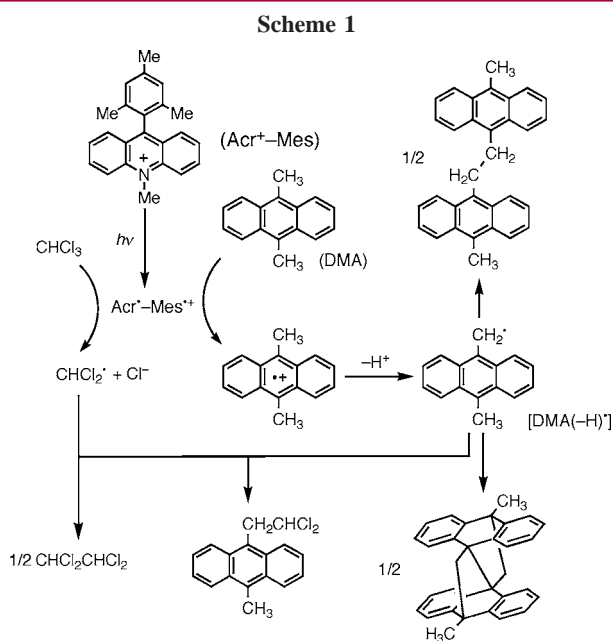
Further improvement of the product yield can be achieved by the addition of a base such as tetrabutylammonium hydroxide (TBAOH), which accelerates deprotonation of DMA^{•+}. When TBAOH was introduced to a CHCl₃ solution containing DMA and Acr[•]–Mes, the isolated yield of dimethyllepidoptere was increased to 21%, as compared with the yield in the absence of base (12%).

In conclusion, Acr[•]–Mes acts as an efficient photocatalyst for the formation of dimethyllepidoptere from 9,10-dimethylantracene in chloroform, which proceeds via the radical coupling of 9-methylanthryl-10-methyl radical.

Acknowledgment. This work was partially supported by a Grant-in-Aid (no. 17750039) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Crystallographic information in CIF format; ¹H NMR, ¹³C NMR, and EI-MS spectra of dimethyllepidoptere; and transient absorption measurements for the reduction of CHCl₃. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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dimethyllepidoptere together with 1,2-bis(9-anthracenyl)ethane.^{29,30}

The Acr[•] moiety of Acr[•]–Mes, which is produced by electron transfer from DMA to Acr[•]–Mes^{•+}, may be oxidized

(25) The decay of Acr[•]–Mes^{•+} in acetonitrile obeyed second-order kinetics because Acr[•]–Mes^{•+} disappears by intermolecular back electron transfer between electron-transfer states at room temperature.^{18a}

(26) Kavarnos, G. J. In *Fundamental of Photoinduced Electron Transfer*; Wiley-VCH: New York, 1993.

(27) (a) Tolbert, L. M.; Khanna, R. K.; Popp, A. E.; Gelbaum, L.; Bottomley, L. A. *J. Am. Chem. Soc.* **1990**, *112*, 2373. (b) Zhao, Y.; Lu, Y.; Parker, V. D. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1481.

(28) The transient absorption spectrum of (DMA-H)[•] is not observed in the monitored wavelength range in Figure 4.¹⁶

(29) Benniston et al. reported that the triplet energy (1.96 eV) of the Acr[•] moiety was lower than the electron-transfer state (2.37 eV).³⁰ Such a triplet excited state would lead to formation of anthracene [4 + 4]-cycloadduct rather than lepidoptere via the triplet excited state of anthracene produced by energy transfer. In fact, the reported triplet state is shown to derive from the acridine impurity.^{18b}

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