

withdrawal from the electron-deficient transition state, but the preference for inside vs. outside probably occurs in order to minimize the repulsions between the allylic oxygen and the nitrile oxide oxygen. The reaction of 3-methoxy-3,4,4-trimethyl-1-pentene with PNBNO gives a 91:9 preference for the product with *t*-Bu anti, Me outside, and OMe inside. This also reflects the operation of the "inside alkoxy" effect. This effect causes an alkoxy group to be effectively larger than a methyl group, with respect to the oxygen of a nitrile oxide.

Model A is also appropriate for the major products of OsO<sub>4</sub> hydroxylations.<sup>1c-f</sup> The preferred product comes from A, with M = OH or OR and L = alkyl. We have also investigated the OsO<sub>4</sub> hydroxylation of alkene **2d**. Under standard conditions,<sup>1c</sup> two products are formed in a 90:10 ratio, the major product arising from A. Vedejs and McClure have discovered many examples which follow this model and show no indication of the operation of electronic effects.<sup>1f,6</sup>

Model A is the same as the Felkin-Anh version of Cram's rule for nucleophilic additions.<sup>7</sup> Other electrophilic reactions give the opposite stereochemical preference. Hydroborations with bulky alkylboranes or of *cis*-alkenes prefer model B, since the inside position is now more crowded than the outside. Reactions of electrophiles with chiral enolates also occur via B, most likely because these have very early transition structures, with geometries and conformations resembling those of reactants.<sup>1f</sup>

Structure **5** is the MM2 model for the transition state leading to the major product of reaction of **2e**. This is more stable than **6**, because the latter cannot simultaneously avoid methyl-O and *t*-Bu-CH<sub>2</sub> repulsions. Models **5** and **6** are very product-like with

respect to the conformations about the bonds to the alkene. Indeed, X-ray crystal structures of products resemble the transition-state models to a remarkable degree. For example, **7** is the crystal structure of the major product of the reaction of **1** with **2e**. As in A, the largest alkyl group is anti, and the smaller alkyl group is inside. Thus, although the transition states are relatively early in terms of bond making and bond breaking, they are very product-like in terms of conformational preferences.<sup>5</sup>

**Acknowledgment.** We are grateful to the National Institutes of Health for financial support of this research and to Professor Edwin Vedejs for discussions and valuable suggestions.

**Supplementary Material Available:** X-ray data for **7**, including a stereo plot and tables of atomic coordinates, isotropic thermal parameters, bond distances and angles, and torsion angles (9 pages). Ordering information is given on any current masthead page.

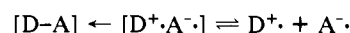
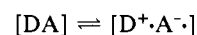
### Oxygenation and [3 + 2] Cycloaddition of Methylene-cyclopropanes through Electron Donor-Acceptor Complexes with Tetracyanoethylene by Photoexcitation and in the Dark<sup>1</sup>

Tsutomu Miyashi,\* Masaki Kamata, and Toshio Mukai

Photochemical Research Laboratory, Faculty of Science  
Tohoku University, Sendai 980, Japan

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Recently, Kochi, Rentzepis, and co-workers spectroscopically demonstrated that the photoexcitation of electron donor-acceptor (EDA) complexes [DA] initially forms geminate radical ion pairs [D<sup>+</sup>·A<sup>-</sup>].<sup>3a</sup> Time-resolved spectroscopic studies by Kochi and co-workers further demonstrated that two processes, a rapid cage process to form adducts D-A and diffusion to solvent-separated radical cations D<sup>+</sup>, competitively occur through [D<sup>+</sup>·A<sup>-</sup>].<sup>3b</sup>



Those intriguing spectroscopic observations prompted us to report our findings that oxygenation of methylene-cyclopropanes (MCP) and the [3 + 2] cycloaddition of MCP with tetracyanoethylene (TCNE) through the EDA complexes with TCNE occurred not only by the photoexcitation but also in the dark. Herein we report clear-cut experimental observations that those two processes occurred independently through two different intermediates, significantly depending on the solvent polarity.

2,2-Diaryl-1-methylene-cyclopropanes (**1a-c**) formed colored EDA complexes when mixed with TCNE in dry CH<sub>2</sub>Cl<sub>2</sub>.<sup>4</sup> When a colored solution of **1a** with TCNE in oxygen-saturated CH<sub>2</sub>Cl<sub>2</sub> was irradiated (>390 nm) for 1 h at 20 °C, dioxolanes **2a**<sup>5a</sup> and **3a**<sup>5a</sup> were obtained together with cycloadducts **4a**<sup>6</sup> and **5a**.<sup>6</sup>

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(4) Charge-transfer absorption maxima of EDA complexes of **1** with TCNE in CH<sub>2</sub>Cl<sub>2</sub> were 370 and 568 nm for **1a**, 388 and 540 nm for **1b**, 366 and 490 nm for **1c**, and 398 nm for **1d**.

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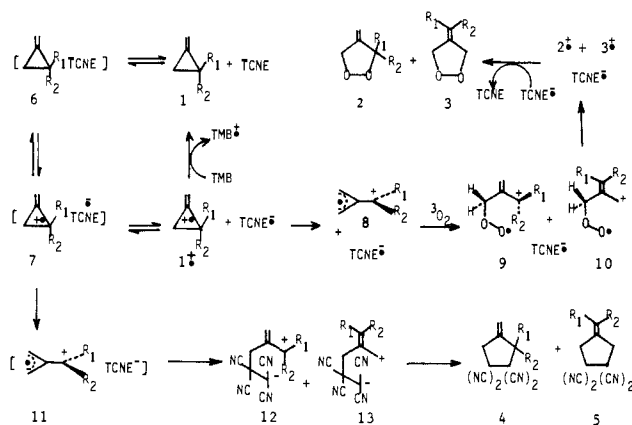
(6) Our MM2 model predicts that the alkoxy-anti, alkyl-outside conformation is preferred in the OsO<sub>4</sub> reactions of *cis*-disubstituted alkenes, as has been proposed by Vedejs.<sup>1f</sup>

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**Table I.** Yields of Dioxolanes (**2** and **3**) and [3 + 2] Cycloadducts (**4** and **5**) from **1** under Irradiation and in the Dark in Oxygen-Saturated Solvents

MCP	solvent	yields <sup>a</sup>									
		irradiated <sup>b</sup>				conv <sup>a</sup>	dark <sup>c</sup>				
		2	3	4	5		2	3	4	5	conv <sup>a</sup>
<b>1a</b>	C <sub>6</sub> H <sub>6</sub>	8	<i>f</i>	57	27	100	0	0	18	29	57 <sup>e</sup>
<b>1a</b>	C <sub>6</sub> H <sub>6</sub>	42	<i>f</i>	36	18	100	38	<i>f</i>	8	39	86 <sup>e</sup>
<b>1b</b>	CH <sub>2</sub> Cl <sub>2</sub>	26	<i>f</i>	40	32	100	8	<i>f</i>	4	7	20 <sup>d</sup>
<b>1c</b>	CH <sub>2</sub> Cl <sub>2</sub>	25	4	34	34	100	4	3	0	3	12 <sup>d</sup>
<b>1a</b>	CH <sub>3</sub> NO <sub>2</sub>	92	0	0	<i>f</i>	100	90	0	0	<i>f</i>	100 <sup>e</sup>
<b>1a</b>	CH <sub>3</sub> NO <sub>2</sub>	86	0	0	<i>f</i>	100	99	0	0	<i>f</i>	100 <sup>e</sup>
<b>1b</b>	CH <sub>3</sub> CN	78	0	8	<i>f</i>	92	42	0	<i>f</i>	<i>f</i>	44 <sup>e</sup>
<b>1c</b>	CH <sub>3</sub> CN	55	4	17	13	91	14	0	0	<i>f</i>	18 <sup>e</sup>

<sup>a</sup> Yields (%) and conversions (%) were determined by 90-MHz NMR using *tert*-butylbenzene as an internal standard. <sup>b</sup> [1] = [TCNE] = 0.10 mM in 3 mL of solvent; irradiation time, 1 h. <sup>c</sup> [1] = [TCNE] = 0.10 mM in 3 mL of solvent. <sup>d</sup> Stirred at 20 °C for 2 days in the dark. <sup>e</sup> Stirred at 20 °C for 7 days in the dark. <sup>f</sup> Less than 2% yield.

**Scheme I**

a: R<sub>1</sub>=R<sub>2</sub>=*p*-MeOC<sub>6</sub>H<sub>4</sub>; b: R<sub>1</sub>=*p*-MeOC<sub>6</sub>H<sub>4</sub>, R<sub>2</sub>=C<sub>6</sub>H<sub>5</sub>; c: R<sub>1</sub>=R<sub>2</sub>=*p*-MeC<sub>6</sub>H<sub>4</sub>; d: R<sub>1</sub>=R<sub>2</sub>=C<sub>6</sub>H<sub>5</sub>

Similar photochemical results obtained for **1b**<sup>7</sup> and **1c**<sup>8</sup> were shown in Table I. Although yields were low for the less electron-donative **1b** and **1c**,<sup>9</sup> it was particularly remarkable that the same oxygenation and [3 + 2] cycloaddition took place even in the dark as shown in Table I. One interesting common feature in the photoexcitation and dark reactions was the suppression of oxygenation by 1,2,4,5-tetramethoxybenzene (TMB) as a quencher. Addition of TMB suppressed oxygenation almost completely but not the [3 + 2] cycloaddition at all.<sup>10</sup> Those results indicate the independent occurrences of two competitive pathways through

(6) Satisfactory elemental analyses were obtained for all new compounds in this report. **2a** and **3a** are known.<sup>5a</sup> Since **4a** easily rearranged to **5a** on silica gel, **4a** could not be isolated. But, **4a** was easily characterized by the NMR spectrum. **4a**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz) δ 3.70 (2 H, m), 3.75 (6 H, s), 5.49 (1 H, m), 5.70 (1 H, m), 6.80–7.10 (4 H, m), 7.20–7.50 (4 H, m). **5a**: mp 151–152 °C; mass spectrum, *m/e* (25 eV) 394 (M<sup>+</sup>, 67%), 266 (100%); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz) δ 3.51 (4 H, s), 3.72 (6 H, s), 6.75–7.20 (8 H, m).

(7) **2b**: oil; mass spectrum, *m/e* (25 eV) 268 (M<sup>+</sup>, 38%), 210 (100%), 135 (94%), 105 (65%); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz) δ 3.78 (3 H, m), 4.87 (3 H, m), 5.29 (1 H, m), 6.75–7.50 (9 H, m). **4b**: mp 145–146 °C; mass spectrum, *m/e* (25 eV) 364 (M<sup>+</sup>, 58%), 236 (100%); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz), δ 3.71 (2 H, m), 3.80 (3 H, s), 5.53 (1 H, m), 5.70 (1 H, m), 6.75–7.10 (2 H, m), 7.10–7.50 (7 H, m). **5b**: mp 124–125 °C; mass spectrum, *m/e* (25 eV) 364 (M<sup>+</sup>, 63%), 236 (100%); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz) δ 3.48 (2 H, s), 3.54 (2 H, s), 3.80 (3 H, s), 6.70–7.60 (9 H, m).

(8) **2c** and **3c** are known.<sup>5a</sup> **4c**: mp 180–181 °C; mass spectrum, *m/e* (25 eV) 362 (M<sup>+</sup>, 24%), 234 (74%), 219 (100%); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz) δ 2.36 (6 H, s), 3.70 (2 H, m), 5.54 (1 H, m), 5.68 (1 H, m), 7.06–7.33 (8 H, m). **5c**: mp 169–170 °C; mass spectrum, *m/e* (25 eV) 362 (M<sup>+</sup>, 31%), 234 (48%), 219 (100%); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz) δ 2.34 (6 H, s), 3.50 (4 H, s), 6.95–7.25 (8 H, m).

(9) The half-wave oxidation potentials of **1** measured by cyclic voltammetry at a platinum electrode in CH<sub>3</sub>CN with 0.1 M tetraethylammonium perchlorate as a supporting electrolyte are 1.35 V for **1a**, 1.46 V for **1b**, 1.65 V for **1c**, and 1.83 V vs. SCE for **1d**.

(10) The calculated Δ*G* values for the reactions of TMB with 1<sup>+</sup> are -10.4, -12.9, and -17.3 kcal/mol, respectively, for **1a-c**.

two different intermediates in both the photoexcitation and dark reactions.

By combination of those experimental results with our previous studies on trimethylenemethane cation radicals **8**,<sup>5</sup> the electron-transfer mechanism shown in Scheme I can be proposed. Irradiation of EDA complexes **6** initially forms geminate radical ion pairs **7**, much more efficiently than the dark reaction. **7** successively collapses in two different pathways. One is diffusion to 1<sup>+</sup> and TCNE anion radical. The other is the ring cleavage within the solvent cage to form ring-opened geminate radical ion pairs **11**. The suppression of oxygenation by TMB should be ascribed to electron transfer from TMB to 1<sup>+</sup>.<sup>10</sup> Since electron transfer from TCNE anion radical to triplet oxygen is highly endothermic,<sup>11</sup> triplet molecular oxygen likely captured **8**<sup>5b</sup> to give dioxolanes.<sup>5a</sup> The back electron transfer from TCNE anion radical to 2<sup>+</sup> and 3<sup>+</sup> then completes the oxygenation cycle, regenerating TCNE, which, in turn, reenters the EDA complex formation cycle. On the other hand, the [3 + 2] cycloaddition rapidly occurs within the solvent cage through **11**. The following evidences further supported this mechanism.

If this mechanism is valid, the solvent polarity and electron-donative nature of a donor substrate should be significant for both reaction pathways as was suggested by time-resolved spectroscopic studies.<sup>3b</sup> Diffusion of **7** to 1<sup>+</sup> followed by the ring cleavage to **8** should be highly favored in the more polar solvent, whereas the rate-determining ring cleavage of **7** to **11** should be obviously less sensitive to the solvent polarity since it occurs within the solvent cage.

As shown in Table I, the dramatic solvent effects on the product ratio were observed for **1a** in both the photoexcitation and dark reactions. Two reaction pathways competed in CH<sub>2</sub>Cl<sub>2</sub>, but oxygenation which was a minor pathway in the less polar benzene became an exclusive pathway in the more polar CH<sub>3</sub>NO<sub>2</sub> and CH<sub>3</sub>CN. On the other hand, the solvent effect on the [3 + 2] cycloaddition observed in the photoexcitation of the EDA complex of **1d** with TCNE under nitrogen<sup>12</sup> was in good accord with the previously reported one for the thermal [3 + 2] cycloaddition of **1d** with TCNE,<sup>13</sup> indicating that the solvent polarity is of no importance for the [3 + 2] cycloaddition. Increases in yields of oxygenation with an increase in the electron-donative nature of **1** in CH<sub>3</sub>CN can be explained by the assertion<sup>3b</sup> that diffusion from **7** to 1<sup>+</sup> occurs much more efficiently in the EDA complexes of the more electron-donative substrates. Those experimental results also support that diffused radical cations **8** don't enter the [3 + 2] cycloaddition manifold and that the [3 + 2] cycloaddition occurs only through **11** within the solvent cage.

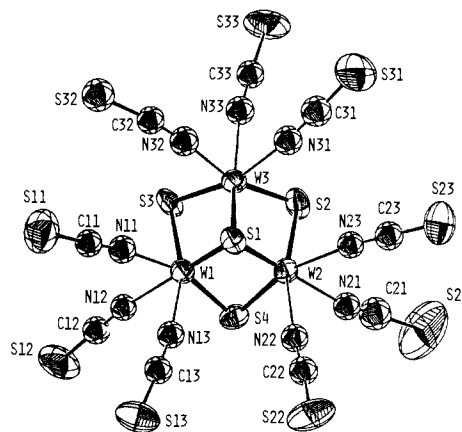
(11) The calculated Δ*G* value for the reaction of triplet oxygen with TCNE anion radical is 30.9 kcal/mol.

(12) The total yields of **4d** and **5d** from **1d** were 34% (37% conversion) in benzene, 79% (80% conversion) in CH<sub>2</sub>Cl<sub>2</sub>, 31% 33% conversion) in CH<sub>3</sub>NO<sub>2</sub>, and 37% (38% conversion) in CH<sub>3</sub>CN when irradiated for 1 h under nitrogen.

(13) The thermal [3 + 2] cycloaddition of **1d** with TCNE to give **4d** (35%) and **5d** (45%) was reported to occur through a concerted [2 + 2 + 2] cycloaddition mechanism. See: Noyori, R.; Hayashi, N.; Kato, M. *J. Am. Chem. Soc.* **1971**, *93*, 4948.

The results described here thus experimentally demonstrated that diffused radical cations behave differently from geminate radical ion pairs and that the solvent polarity is remarkably important for reactions that proceed through EDA complexes. It is also of interest to note that the present observation of oxygenation in the dark is the first example of oxygenation through EDA complexes with TCNE and undoubtedly verified an electron-transfer mechanism for the thermal [3 + 2] cycloaddition of MCP with TCNE, which was previously explained by a simple concerted [2 + 2 + 2] cycloaddition mechanism.<sup>13</sup> Similar results which supplement the proposed mechanism have been obtained in the photoexcitations of the EDA complexes of three-membered compounds such as 1,1,2,2-tetraarylcyclopropanes, 2,3-diaryl-oxiranes, and 2,3-diarylaziridines with TCNE in oxygen-saturated solvents. Those detail results will be soon reported.

**Acknowledgment.** Financial support from Kurata Foundation is gratefully acknowledged.



**Figure 1.** Perspective view of  $[W_3S_4(NCS)_9]^{5-}$  with selected bond distances (Å): W1--W2, 2.767 (2); W1--W3, 2.766 (2); W2--W3, 2.761 (2); W1--S1, 2.355 (9); W2--S1, 2.384 (9); W3--S1, 2.354 (9); W1--S3, 2.320 (10); W1--S4, 2.313 (9); W2--S2, 2.313 (11); W2--S4, 2.310 (9); W3--S2, 2.304 (11); W3--S3, 2.289 (10); W--N, 2.154 (av).

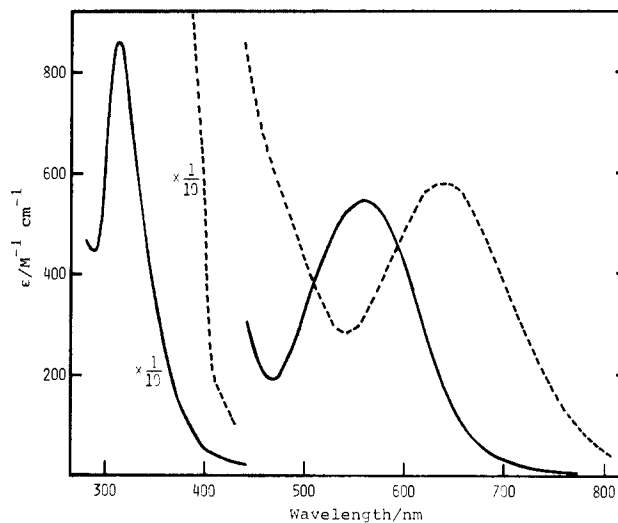
### Preparation of Triangular Tungsten(IV) Aqua Ion, $W_3S_4^{4+}$ , and X-ray Structure of $(bpyH)_5[W_3S_4(NCS)_9] \cdot 3H_2O$

Takashi Shibahara,\* Katsumi Kohda, Akiko Ohtsuji, Kohichi Yasuda, and Hisao Kuroya

Department of Chemistry, Okayama University of Science, 1-1 Ridai-cho, Okayama 700, Japan

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Many reports have been made on the trinuclear tungsten compounds, in which tungsten atoms are bridged by several kinds of atoms or ligands, i.e.,  $\mu_3-O$ ,  $\mu_3-CMe$ ,  $\mu_3-O-i-Pr$ ,  $\mu_3-As$ ,  $\mu_3-NH$ ,  $\mu_3-Cl$ ,  $\mu_2-O$ ,  $\mu_2-O-i-Pr$ , and/or  $\mu_2-O_2CR$ .<sup>1</sup> A molecular orbital treatment of the triangular compounds has also been published.<sup>2</sup> Quite recently preparation and characterization of a tungsten(IV) aqua ion,  $W_3O_4^{4+}$ , has been reported.<sup>3</sup> However, no report on triangular tungsten compounds with any sulfur bridge, including the triangular tungsten(IV) aqua ion,  $W_3S_4^{4+}$ , has been published previously.<sup>4</sup> Preparation and characterization of molybdenum(IV) aqua ions with and without sulfur bridge(s),  $Mo_3O_4^{4+}$ ,<sup>5</sup>  $Mo_3O_3S^{4+}$ ,<sup>6</sup>  $Mo_3O_2S_2^{4+}$ ,<sup>7</sup>  $Mo_3OS_3^{4+}$ ,<sup>8</sup> and  $Mo_3S_4^{4+}$ ,<sup>9</sup> have been worked out<sup>10</sup>



**Figure 2.** Electronic spectra: (—)  $W_3S_4^{4+}$  in 2 M HPTS; (---)  $[W_3S_4(NCS)_9]^{5-}$  in 1 M HCl containing 1 M KSCN.

and the presence of incomplete cubane-type  $Mo_3O_4-nS_n^{4+}$  core ( $n = 0-4$ ) has been revealed by X-ray structure analyses of compounds derived from those aqua ions and appropriate ligands.<sup>5-9</sup> Detailed electrochemical studies of  $Mo_3O_4^{4+}$  aqua ion have also been carried out.<sup>11</sup>

We describe here the preparation and characterization of the incomplete cubane-type  $W_3S_4^{4+}$  aqua ion and X-ray structure analysis of a derivative complex  $(bpyH)_5[W_3S_4(NCS)_9] \cdot 3H_2O$  (bpy; 2,2'-bipyridine).

Sodium borohydride (3 g in 20 mL of  $H_2O$ ) and HCl (6 M, 20 mL) were pipetted alternately into a yellow solution of  $(NH_4)_2WS_4$ <sup>12</sup> (3 g in 500 mL of  $H_2O$ ) at room temperature. Another quantity of HCl (6 M, 80 mL) was added to the resultant dark brown solution, through which air was passed at ca. 80 °C for 12 h. One molar HCl was added occasionally to the solution during air oxidation, in order to keep the volume of the solution at ca. 200 mL. After it was cooled to room temperature, the solution was filtered and Sephadex G-15 column chromatography was applied (1 M HCl). The third blue-violet band ( $\lambda_{max} = 570$  nm in 1 M HCl)<sup>13</sup> obtained by the procedure was purified by use

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