It has been found by Jordan that the effective pH of HCl in aqueous acetonitrile may be approximated by -log [HCl].[25a] For the buffer and NaOH solutions in 50% CH_3CN, corrections derived by McGall and McClelland[25b] at 25 °C and μ = 0.25 were found to also be valid at μ = 0.05 and were applied to our measured pH values. For buffers, pH = pH_{meas} + 0.18, where the factor 0.18 accounts for the difference in the medium from pure H_2O, and for NaOH, pH = 15.0 + log [NaOH], where 15.0 is the pK_w determined for H_2O in this medium.

(25) (a) Jordan, F. *J. Phys. Chem.* **1973**, *77*, 2681-2683. (b) McGall, G.; McClelland, R. A., University of Toronto, unpublished results privately communicated.

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Simultaneous Capture of Two Distinct Radical Ion Intermediates Generated from the EDA Complexes of Three-Membered Compounds with TCNE by Photoexcitation and in the Dark[1]

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Abstract: Irradiation of the electron donor-acceptor (EDA) complexes of 2,2-diaryl-1-methylenecyclopropanes, 1,1,2,2-tetraarylcyclopropanes, 2,3-diaryloxiranes, or 2,3-diarylaziridines with tetracyanoethylene (TCNE) under aerated conditions involved oxygenation and/or the [3 + 2] cycloaddition with TCNE. The same oxygenation took place in the dark when the EDA complexes of 2,2-diaryl-1-methylenecyclopropanes or 1,1,2,2-tetraarylcyclopropanes with TCNE were simply stirred in oxygen-saturated solvents. Oxygenation occurred much more efficiently as the solvent polarity and the electron-donative nature of donor substrates increased. 1,2,4,5-Tetramethoxybenzene (TMB) used as a quencher efficiently suppressed oxygenation but not the [3 + 2] cycloaddition at all. Oxygenation occurs through the solvent-separated radical cations diffused from the photogenerated geminate radical ion pairs, whereas the cage coupling of the radical ion pairs involves the [3 + 2] cycloaddition with TCNE.

The electron-transfer reactions which proceed through EDA complexes have been recognized as important processes not only in photochemical but also in thermal reactions. In fact, many organic photochemical and thermal reactions initiated by electron donor-acceptor interactions have appeared in literature.[2] Despite that, simple isomerization of donor substrates or donor-acceptor adduct (D-A) formation reactions usually occur,[3] and experimental identifications of resulting radical ion intermediates are often ambiguous, mainly because such reactions may occur via complex multiple processes, all of which do not necessarily participate in the product formation step. Recent time-resolved spectroscopic studies by Hilinski and co-workers spectroscopically demonstrated those and clearly gained insight into an initial step of the photoexcitation of EDA complexes and roles of successively generated radical ion intermediates.[4]

$$[DA] \overset{h\nu}{\rightleftharpoons} [D^{\bullet+}A^{\bullet-}]$$

$$D\text{-}A \leftarrow [D^{\bullet+}A^{\bullet-}] \rightleftharpoons D^{\bullet+} + A^{\bullet-}$$

Interestingly, the irreversible donor-acceptor adduct formation pathway was found to occur competitively with reversible diffusion between the solvent-separated radical cations $D^{\bullet+}$ and the radical ion pairs $[D^{\bullet+}A^{\bullet-}]$. Experimental verification of such processes is thus obviously difficult as long as chemical capture of $D^{\bullet+}$ cannot be simultaneously performed. It may be, however, possible if the photoexcitation of EDA complexes is investigated under conditions in which the D-A formation competitively occurs with chemical capture of $D^{\bullet+}$, such as oxygenation. For this purpose, we thought that strained three-membered compounds such as 2,2-diaryl-1-methylenecyclopropanes (**1**), 1,1,2,2-tetraarylcyclopropanes (**6**), 2,3-diaryloxiranes (**12**), and 2,3-diarylaziridines (**16**) seemed to be suitable as donor substrates since these donors make the EDA complexes with TCNE as shown in Table I, and their electron-transfer oxygenations[5-8] under photosensitized conditions and their

(1) Organic Photochemistry 77. For No. 76, see: Yamashita, Y.; Hanaoka, K.; Mukai, T. *Chem. Lett.* **1986**, 1279.

(2) Foster, T. *Organic Charge-Transfer Complexes*; Academic: New York, 1969, p 303 and references cited therein.

(3) For recent studies on three- and four-membered compounds, for instance, see: Arnold, D. R.; Humphreys, R. W. R. *J. Am. Chem. Soc.* **1979**, *101*, 2743. Mukai, T.; Sato, K.; Yamashita, Y. *J. Am. Chem. Soc.* **1981**, *103*, 670. Jones, G., II; Becker, W. G. *Chem. Phys. Lett.* **1982**, *85*, 271; *J. Am. Chem. Soc.* **1983**, *105*, 1276. Wayer, D. D. M.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 871.

(4) (a) Hilinski, E. F.; Masnovi, J. M.; Amatore, C.; Kochi, J. K.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 6167. Hilinski, E. F.; Masnovi, J. M.; Kochi, J. K.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 8071. (b) Masnovi, J. M.; Levine, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 4356.

(5) Oxygenation of methylenecyclopropanes: (a) Takahashi, Y.; Miyashi, T.; Mukai, T. *J. Am. Chem. Soc.* **1983**, *105*, 6511. (b) Okada, K.; Hisamitsu, K.; Takahashi, Y.; Hanaoka, K.; Miyashi, T.; Mukai, T. *Tetrahedron Lett.* **1984**, *25*, 5311. (c) Miyashi, T.; Takahashi, Y.; Mukai, T.; Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1985**, *107*, 1079.

(6) Oxygenation of cyclopropanes: (a) Schaap, A. P.; Lopez, L.; Anderson, S. D.; Gagnon, S. D. *Tetrahedron Lett.* **1982**, *23*, 5493. (b) Schaap, A. P.; Siddiqui, S.; Prasad, G.; Palomino, E.; Lopez, L. *J. Photochem.* **1984**, *25*, 167. (c) Mizuno, K.; Kamiyama, N.; Otsuji, Y. *Chem. Lett.* **1983**, 477. (d) Mizuno, K.; Kamiyama, N.; Ichinose, N.; Otsuji, Y. *Tetrahedron* **1985**, *41*, 2207.

(7) Oxygenation of oxiranes: (a) Schaap, A. P.; Siddiqui, S.; Balakrishnan, P.; Lopez, L. *Isr. J. Chem.* **1983**, *23*, 415. (b) Schaap, A. P.; Lopez, L.; Gagnon, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 663. (c) Schaap, A. P.; Siddiqui, S.; Gagnon, S. D.; Lopez, L. *J. Am. Chem. Soc.* **1983**, *105*, 5149. (d) Schaap, A. P.; Siddiqui, S.; Prasad, G.; Rahman, A. F. M. M.; Oliver, J. P. *J. Am. Chem. Soc.* **1984**, *106*, 6087. (e) Schaap, A. P.; Siddiqui, S.; Prasad, G.; Palomino, E.; Lopez, L. *J. Photochem.* **1984**, *25*, 167. (f) Schaap, A. P.; Siddiqui, S.; Prasad, G.; Palomino, E.; Sandison, M. *Tetrahedron* **1985**, *41*, 2229. (g) Futamura, S.; Kusunose, S.; Ohta, H.; Kamiya, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 1223. (h) Futamura, S.; Kusunose, S.; Ohta, H.; Kamiya, Y. *J. Chem. Soc., Perkin Trans. 1* **1984**, 15. (i) Kirschenheuter, G. P.; Griffin, G. W. *J. Chem. Soc., Chem. Commun.* **1983**, 596.

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Table I. Half-Wave Oxidation Potentials and Charge-Transfer Absorptions

compd	X	Y	Z	$E^{ox}_{1/2}$, V vs. SCE	CT absorption, nm in CH_2Cl_2	
1a	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$		1.35	370	568
1b	*p*-$MeOC_6H_4$	C_6H_5		1.46	388 (sh)	540
1c	*p*-MeC_6H_4	*p*-MeC_6H_4		1.65	366	490
1d	C_6H_5	C_6H_5		1.83	398	
1e	*p*-ClC_6H_4	*p*-ClC_6H_4		1.88	436 (sh)	
6a	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$		0.87	522	
6b	*p*-$MeOC_6H_4$	*p*-MeC_6H_4		0.93	401	552
6c	*p*-$MeOC_6H_4$	C_6H_5		0.94	400	534
6d	*p*-$MeOC_6H_4$	*p*-ClC_6H_4		1.01	386 (sh)	526
6e	*p*-MeC_6H_4	*p*-MeC_6H_4		1.11	410	496 (sh)
6f	C_6H_5	C_6H_5		1.28	401	496 (sh)
trans-**12a**	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$		1.27	380 (sh)	540
trans-**12b**	*p*-$MeOC_6H_4$	*p*-MeC_6H_4		1.42	387	506
cis-**12c**	*p*-$MeOC_6H_4$	C_6H_5		1.47	373	516
trans-**12d**	*p*-$MeOC_6H_4$	*p*-ClC_6H_4		1.47	364 (sh)	518
trans-**12e**	*p*-$MeOC_6H_4$	C_6H_5		1.48	366	520
trans-**12f**	*p*-$MeOC_6H_4$	*p*-$NO_2C_6H_4$		1.53	520	
trans-**12g**	*p*-MeC_6H_4	*p*-MeC_6H_4		1.61	390	460 (sh)
trans-**12h**	C_6H_5	C_6H_5		1.82	374	
trans-**16a**	H	C_6H_5	$CH_2C_6H_5$	1.50	401	420
cis-**16b**	C_6H_5	H	$CH_2C_6H_5$	1.61	402	
cis-**16c**	C_6H_5	H	*n*-butyl	1.65	410	
cis-**16d**	C_6H_5	H	Me	1.70	420	

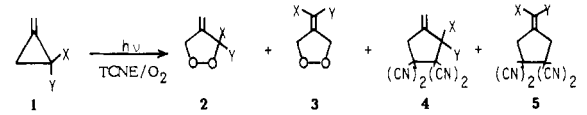
[3 + 2] cycloadditions[9,10] with TCNE are known. Furthermore, in connection with mechanisms of the previously reported photosensitized electron-transfer oxygenations of those donor substrates,[5-8] it was also of interest to clarify the oxygen species and structures of intermediate donor radical cation counterparts directly relevant to the oxygenation step. Since reported photosensitized oxygenations were mostly investigated under conditions in which not only oxygen anion radical but also singlet oxygen is assumed to be generated from triplet oxygen by electron transfer, the experimental identification of the oxygen species seems to be difficult. In contrast, the photoexcitation of EDA complexes with TCNE under aerated conditions does not involve such oxygen species. Thus, if those donors are expectedly oxygenated, comparisons of results with those of the photosensitized oxygenations would be valued to gain insight into mechanisms of the photosensitized electron-transfer oxygenations.[5-8]

For those purposes, we investigated the photoexcitation and dark reactions of the EDA complexes of 23 donors listed in Table I with TCNE under aerated conditions, changing the solvent polarity and the electron-donative nature of donor substrates.

Herein we report clear-cut experimental observations which demonstrated that two distinct intermediates were independently intercepted by triplet oxygen and TCNE, giving oxygenation and [3 + 2]-cycloaddition products, respectively. In addition, the solvent polarity and the electron-donative nature of donor substrates were found to be remarkably important for oxygenation which occurred not only by the photoexcitation but also in the dark.

Results

The symmetrically and unsymmetrically substituted three-membered compounds **1**, **6**, **12**, and **16** exhibited absorptions in the visible region due to charge transfer when mixed with TCNE in dichloromethane as shown in Table I. The electron-donative nature of those donor substrates was increased by the introductions of the more electron-donative substituents. However, the oxidation potentials did not simply correlate with the simple sum of two σ_p^+ values, $[\sigma_p^+(X) + \sigma_p^+(Y)]$, where X is more electron-donative than Y, but linearly correlated with the weighed sum of two substituent constants. For instance, in a series of **12**, the oxidation potentials ($E^{ox}_{1/2}$) nicely correlated with the Hammett equation, $0.64[0.76\sigma_p^+(X) + 0.24\sigma_p^+(Y)] + 1.82$ ($r = 0.980$), indicating major contribution of X to the electron-donative nature of the unsymmetrically substituted **12**. Thus, **12f** substituted with the *p*-methoxyphenyl and *p*-nitrophenyl groups appeared to be more electron donative than **12g** and **12h**. Similar Hammett relations, $0.60[0.78\sigma_p^+(X) + 0.22\sigma_p^+(Y)] + 1.83$ ($r = 0.999$) and $0.53[0.75\sigma_p^+(X) + 0.25\sigma_p^+(Y)] + 1.28$ ($r = 0.993$), were derived for oxidation potentials of **1** and **6**, respectively.



(1)

1 **2** **3** **4** **5**

a, X = Y = *p*-$MeOC_6H_4$; **b**, X = *p*-$MeOC_6H_4$, Y = C_6H_5; **c**, X = Y = *p*-MeC_6H_4; **d**, X = Y = C_6H_5; **e**, X = Y = *p*-ClC_6H_4.

Upon irradiation of the EDA complex of **1a** (0.10 mmol) with TCNE (0.10 mmol) with light more than 390 nm at 20 °C in oxygen-saturated dichloromethane (3 mL) for 1 h, **1a** was quantitatively consumed and dioxolanes **2a** and **3a**[5] were obtained together with [3 + 2] cycloadducts **4a** and **5a** in excellent yields as shown in Table II together with similar results obtained for **1b–1e**. The remarkable solvent effects were observed when the irradiations were carried out in the more or less polar solvents as shown in Tables II and III. Oxygenation, in general, occurred much more efficiently in the more polar solvent such as acetonitrile or nitromethane, especially for **1a–1c** with relatively low oxidation potentials, whereas in the less polar benzene the [3 + 2] cycloaddition with TCNE was the exclusive pathway. It was, however, found that the [3 + 2] cycloaddition was not sensitive to the solvent polarity. When the EDA complex of **1d** was irradiated under nitrogen, the conversion of **1d** and the yields of **4d** and **5d** were found not to depend on the order of the solvent polarity as shown in Table III. It is mechanistically noteworthy that similar solvent effects were previously reported for the thermal [3 + 2] cycloaddition of **1d** with TCNE in the dark.[9a]

One particularly intriguing finding was that 1,2,4,5-tetramethoxybenzene (TMB)[11] used as a quencher completely suppressed oxygenation but not the [3 + 2] cycloaddition at all, as shown in Table II. In contrast, anisole (AN) did not significantly affect both reactions.[11] In order to gain further the more gen-

(8) Oxyenation of aziridines: (a) Schaap, A. P.; Prasad, G.; Gagnon, S. D. *Tetrahedron Lett.* **1985**, *24*, 3047. (b) Schaap, A. P.; Prasad, G.; Siddiqui, S. *Tetrahedron Lett.* **1984**, *25*, 3035. (c) Schaap, A. P.; Siddiqui, S.; Prasad, G.; Palomino, E.; Lopez, L. *J. Photochem.* **1984**, *25*, 167.

(9) (a) [3 + 2] cycloaddition of methylenecyclopropanes with TCNE: (a) Noyori, R.; Hayashi, N.; Kato, M. *J. Am. Chem. Soc.* **1971**, *93*, 4948. (b) [3 + 2] cycloaddition of cyclopropanes with TCNE: Martini, Th.; Kampmeier, J. A. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 236. Wiering, P. G.; Steinberg, H. *J. Org. Chem.* **1981**, *46*, 1663.

(10) [3 + 2] cycloaddition of aziridines: Huisgen, R.; Scheer, W.; Maeder, H. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 602. Dominh, T.; Trozzolo, A. M. *J. Am. Chem. Soc.* **1970**, *92*, 6997.

Table II. Yields of Dioxolanes (**2** and **3**) and the Cycloadducts (**4** and **5**) and Effects of Quenchers (TMB and AN)[a]

		yield in dichloromethane, %						yield in acetonitrile, %				
compd	quencher	**2**	**3**	**4**	**5**	con[c]	quencher	**2**	**3**	**4**	**5**	con[c]
1a	none	42	*b*	36	18	100	none	86	0	0	*b*	100
	TMB	0	0	38	27	74						
	AN	36	0	30	19	100						
1b	none	26	*b*	40	32	100	none	78	0	8	*b*	92
	TMB	0	0	38	36	74						
	AN	33	*b*	35	29	100						
1c	none	25	4	34	34	100	none	55	4	17	13	91
	TMB	0	0	41	52	93						
	AN	13	3	40	43	100						
1d	none	8	*b*	34	43	90	none	20	3	12	18	54
	TMB	0	0	28	40	70						
	AN	*b*	*b*	34	42	78						
1e	none	24	4	22	31	87	none	28	*b*	8	11	60
	TMB	0	0	12	19	47						
	AN	7	*b*	14	27	55						

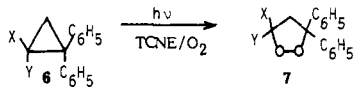
[a] **1**, TCNE, TMB, AN: 0.1 mmol in 3 mL of solvent. [b] Less than 2% yield. [c] Conversion after 1 h of irradiation.

Table III. Yields of Dioxolanes (**2a** and **3a**) and Cycloadducts (**4a** and **5a**) from **1a** under Oxygen and Yields of Cycloadducts (**4d** and **5d**) from **1d** under Nitrogen in Various Solvents[a]

	yield from **1a** under oxygen, %					yield from **1d** under nitrogen, %		
solvent	**2a**	**3a**	**4a**	**5a**	con[c]	**4d**	**5d**	con[c]
benzene	8	*b*	57	27	100	16	18	37
dichloromethane	42	*b*	36	18	100	35	44	80
nitromethane	92	0	0	*b*	100	15	16	33
acetonitrile	86	0	0	*b*	100	17	20	38

[a] **1**, TCNE: 0.1 mmol in 3 mL of solvent. [b] Less than 2% yield. [c] Conversion after 1 h of irradiation.

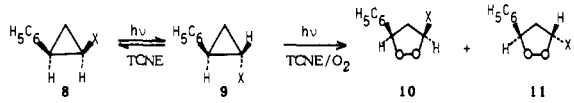
eralized experimental informations for oxygenation through EDA complexes, the photoexcitations of the EDA complexes of cyclopropanes **6**,[12] **8**, and **9** with TCNE were investigated in various oxygen-saturated solvents. As shown in Table IV, oxygenation[14]



(2)

a, X = Y = *p*-$MeOC_6H_4$; **b**, X = *p*-$MeOC_6H_4$, Y = *p*-MeC_6H_4; **c**, X = *p*-$MeOC_6H_4$, Y = C_6H_5; **d**, X = *p*-$MeOC_6H_4$, Y = *p*-ClC_6H_4; **e**, X = Y = *p*-MeC_6H_4; **f**, X = Y = C_6H_5.

of **6** exclusively took place without regard to the solvent polarity, but the yields of **7** increased as the solvent polarity and the electron-donative nature of **6** increased, reconfirming importance of the solvent polarity and the electron-donative nature for oxygenation. Interestingly, the amounts of TCNE did not significantly change the yields of oxygenation. The efficient reaction quenchings by TMB were similarly observed for oxygenations of **6a–6e** as shown in Table IV.[15] The charge-transfer absorptions

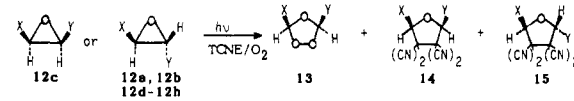


(3)

X = *p*-$MeOC_6H_4$.

with TCNE appeared at 402 and 575 nm for **8** ($E^{ox}_{1/2}$ = 1.42 V vs. SCE) and at 394 and 592 nm for **9** ($E^{ox}_{1/2}$ = 1.22 V vs. SCE) in dichloromethane. A photostationary mixture of **8** and **9** in the ratio 5:95 was obtained upon separate irradiation of the EDA complex of **8** or **9** under nitrogen in dichloromethane, nitromethane, or acetonitrile. On the other hand, upon irradiation of the EDA complex of **9** with TCNE in oxygen-saturated nitromethane for 10 h, *cis*-**10** and *trans*-dioxolane **11**[6c,d] were obtained in 53% and 18% yields, respectively. Both oxygenation and cis—trans isomerization were similarly suppressed by TMB.[16] It is noteworthy that the ratio of **10** and **11** was exactly same as that observed in the 9,10-dicyanoanthracene (DCA)-sensitized oxygenation[6c,d] but significantly differed from the cis–trans isomerization ratio.

Contrastive results between **1** and **6** were of interest. The less thermally stable and electron-donative **1** underwent both oxygenation and the [3 + 2] cycloaddition, whereas the more thermally stable and electron-donative **6** exclusively underwent oxygenation. Thus, we further investigated the photoexcitations of the EDA complexes of oxiranes **12** and aziridines **16** with TCNE, expecting similar contrastive results. The photosensitized electron-transfer oxygenations of **12** and **16** have been reported by Ohta[7g,h] and by Schaap,[7c,d] and careful studies by Schaap have clearly demonstrated that oxygenations of 2,3-diaryloxiranes[7c,d] and 2,3-diarylaziridines[8] occurred stereoselectively under DCA-sensitized conditions. Our additional interest was to know whether oxygenations through EDA complexes stereoselectively occur or not.



(4)

a, X = Y = *p*-$MeOC_6H_4$; **b**, X = Y = *p*-$MeOC_6H_4$, *p*-MeC_6H_4; **c**, X = Y = *p*-$MeOC_6H_4$, C_6H_5; **d**, X = Y = *p*-$MeOC_6H_4$, *p*-ClC_6H_4; **e**, X = Y = *p*-$MeOC_6H_4$, C_6H_5; **f**, X = Y = *p*-$MeOC_6H_4$, *p*-$NO_2C_6H_4$; **g**, X = Y = *p*-MeC_6H_4; **h**, X = Y = C_6H_5.

(11) The calculated ΔG values for electron transfer from TMB to $\mathbf{1}^{\bullet+}$ are −10.4, −12.9, −17.3, −21.4, and −22.6 kcal/mol, respectively, for **1a–1e** in dichloromethane when calculated from the equation ΔG = 23.6[$E^{ox}_{1/2}$(TMB$^{\bullet+}$/TMB) − $E^{ox}_{1/2}$($\mathbf{1}^{\bullet+}$/**1**) + 0.16] kcal/mol, where $E^{ox}_{1/2}$(TMB$^{\bullet+}$/TMB) is 0.74 V vs. SCE. Those from AN ($E^{ox}_{1/2}$ = 1.74 V vs. SCE) to $\mathbf{1}^{\bullet+}$ are +12.7, +10.1, +5.8, +1.6, and +0.5 kcal/mol, respectively, for **1a–1e** in dichloromethane.

(12) The photoexcitation of the EDA complex of **6f** with TCNE was reported by Arnold.[13]

(13) Arnold, D. R.; Humpheys, R. W. R. *J. Am. Chem. Soc.* **1979**, *101*, 2743. Wayner, D. D. M.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 871.

(14) The DCA–biphenyl-cosensitized electron-transfer photooxygenation of **6f** to give **7f** was reported by Schaap.[6a,b]

(15) The calculated ΔG values for electron transfer from TMB to $\mathbf{6}^{\bullet+}$ are +0.7, −0.7, −0.9, −2.5, −4.8, and −8.8 kcal/mol, respectively, for **6a–6f** in dichloromethane.

(16) The calculated ΔG values for electron transfer from TMB to $\mathbf{8}^{\bullet+}$ and $\mathbf{9}^{\bullet+}$ are −7.4 and −12.0 kcal/mol, respectively, in dichloromethane. Neither 1,2,4,5-tetramethylbenzene ($E^{ox}_{1/2}$ = 1.68 V vs. SCE) nor AN quenched the cis–trans isomerization at all.

Table IV. Yields of Dioxolanes (**7**) from **6** and Effects of TMB in Various Oxygen-Saturated Solvents

			TCNE (0.1 mmol)			TCNE (0.02 mmol)		
compd (0.1 mmol)	solvent	TMB, mmol	irr time, h	**7**, %	con,[a] %	irr time, h	**7**, %	con,[a] %
6a	benzene	0	1.0	44	100			
	dichloromethane	0	3.0	58	100			
		0.1	3.0	11	39			
	nitromethane	0	0.7	86	100			
	acetonitrile	0	0.7	94	100	0.7	96	100
		0.1	1.0	51	61			
6b	dichloromethane	0	2.0	46	100	2.0	45	100
		0.1	3.0	9	13			
	acetonitrile	0	0.5	97	100	0.5	93	100
		0.1	1.0	40	43			
6c	dichloromethane	0	3.0	53	100	4.0	44	100
		0.1	3.0	0	3			
	acetonitrile	0	0.5	97	100	0.5	97	100
		0.1	1.0	21	24			
6d	dichloromethane	0	3.0	31	100	2.0	30	100
		0.1	3.0	0	2			
	acetonitrile	0	0.5	93	100	0.5	98	100
		0.1	1.0	13	17			
6e	acetonitrile	0	1.0	66	89	1.0	51	84
		0.1	1.0	0	4			
6f	acetonitrile	0	2.0	15	100	1.0	10	74

[a] Conversion.

Table V. Yields of Trioxolane (**13**) and Cycloadducts (**14** and **15**) from **12** and Effects of TMB in Oxygen-Saturated Dichloromethane

				yield, %			
compd (0.1 mmol)	TCNE, mmol	TMB, mmol	irr time, h	**13**	**14**	**15**	con[b]
12a	0.1	0	1	87	*a*	*a*	100
	0.1	0.1	3	0	10	11	24
	0.02	0	3	80	*a*	*a*	100
12b	0.1	0	1	63	8	7	100
	0.1	0.1	3	0	7	6	15
12c	0.1	0	5	47	14	13	91
	0.1	0.1	3	0	10	8	21
	0.05	0	5	30	14	12	87
12d	0.1	0	2	94	*a*	*a*	100
	0.1	0.1	3	0	*a*	*a*	*a*
	0.02	0	3	96	0	0	100
12e	0.1	0	1	99	0	0	100
	0.1	0.1	3	0	4	*a*	5
	0.02	0	3	98	0	0	100
12f	0.1	0	3	94	0	0	100
	0.1	0.1	3	0	*a*	*a*	*a*
12g	0.1	0	4	35	12	21	100
	0.1	0.1	3	0	7	14	24
12h	0.1	0	10	8	6	15	79
	0.1	0.1	10	0	5	10	18

[a] Less than 2% yield. [b] Conversion.

Upon irradiation of the EDA complex of **12a** with TCNE in dichloromethane under nitrogen, the [3 + 2] cycloadducts **14a** and **15a** were afforded in 27% and 26% yields, respectively, after 72% conversion of **12a**, whereas under oxygen, the exclusive product was trioxolane **13a** (87% yield). Similar results obtained for **12b–12h** were also summarized in Table V.[17] Both *cis*-**12c** and *trans*-**12e** gave *cis*-trioxolane **13c**. The DCA-sensitized photooxygenations of **12a-12h** afforded the same trioxolanes, confirming the cis stereochemical assignment.[7c,d] The major pathway was oxygenation to form **13** for the more electron donative **12a–12f**, but the [3 + 2] cycloaddition to form **14** and **15** was predominant for the less electron donative **12g** and **12h**. It was found that the substitution of one of two aryl groups with the *p*-methoxyphenyl group was very effective to involve efficient oxygenation without regard to the nature of the other aryl group. For instance, oxygenation of **12f** was not retarded by the strong electron-withdrawing *p*-nitrophenyl group but instead was more efficient than those of **12g** and **12h**. This substituent effect on the efficiency of oxygenation can be reasonably explained by major contribution of the *p*-methoxyphenyl group in the electron-donative nature as the Hammett relation in oxidation potentials of **12** disclosed. The amounts of TCNE similarly did not significantly change yields of oxygenation. Oxygenations of **12a–12h** were also completely suppressed by TMB.[18] The solvent effects on the two reaction pathways were tested for **12a**. Similar to **1** and **6**, in the less polar benzene, [3 + 2] cycloadducts **14a** and **15a** were obtained as major products in 28% and 25% yields, respectively,

Table VI. Yields (%) of Cycloadducts (**17** and **18**) from **16** in Oxygen-Saturated Dichloromethane

	16a	**16b**	**16c**	**16d**
cis-**17**	17.1	36.6	47.8	12.8
trans-**18**	72.9	62.4	44.2	72.3

(17) The DCA–biphenyl-cosensitized oxygenations of *cis*- and *trans*-2,3-diphenyloxiranes to form *cis*-**13h** were reported by Schaap.[7c] Ohta and coworkers reported that **12g** and **12h** were not oxygenated under DCA-sensitized conditions.[7g,h]

(18) The calculated ΔG values for electron transfer from TMB to $12^{\cdot+}$ are −8.5, −12.0, −13.1, −13.1, −13.4, −14.5, −16.4, and −21.2 kcal/mol, respectively, for **12a–12h** in dichloromethane. 1,4-Dimethoxybenzene ($E^{ox}_{1/2}$ = 1.25 V vs. SCE), 1,2-dimethoxybenzene ($E^{ox}_{1/2}$ = 1.35 V vs. SCE), and 1,3,5-trimethoxybenzene ($E^{ox}_{1/2}$ = 1.48 V vs. SCE) also suppressed oxygenation of **12e**, but neither 1,2,4,5-tetramethylbenzene nor anisole quenched oxygenation in dichloromethane.

Table VII. Yields (%) of Dioxolanes (**2** and **3**) and Cycloadducts (**4** and **5**) from **1** in the Dark

	in dichloromethane					in acetonitrile				
compd	**2**	**3**	**4**	**5**	con[a]	**2**	**3**	**4**	**5**	con[b]
1a	15	*c*	12	22	50	99	0	0	*c*	100
1b	8	*c*	4	7	20	42	0	*c*	*c*	44
1c	4	3	0	3	12	14	0	0	*c*	18

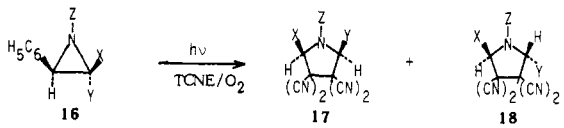
[a] Conversion after stirring for 2 days. [b] Conversion after stirring for 7 days. [c] Less than 2% yield.

Table VIII. Yields of Dioxolanes (**2a** and **3a**) and Cycloadducts (**4a** and **5a**) from **1a** and Effects of Quenchers (TMB and AN) in the Dark[a]

		yield, %				
solvent	quencher	**2a**	**3a**	**4a**	**5a**	con[c]
benzene	none	0	0	18	29	57
dichloromethane	none	38	*b*	8	39	86
	TMB	0	0	5	68	74
	AN	33	0	0	45	86
nitromethane	none	90	0	*b*	0	100
acetonitrile	none	99	0	0	*b*	100

[a] **1a**, TCNE, TMB, AN: 0.10 mmol in 3 mL of solvent. [b] Less than 2% yield. [c] Conversion after stirring for 7 days.

together with a trace of **13a** (3% yield), while in the more polar acetonitrile, **13a** was solely obtained in 65% yield. These experimental observations were common to those observed in the photoexcitations of the EDA complexes of **1** and **6** with TCNE. The most intriguing feature was, however, that the stereoselective oxygenation competitively occurred with the nonstereoselective [3 + 2] cycloaddition. In contrast with the photoexcitations of **1**, **6**, and **12**, those of the EDA complexes of aziridines **16** with TCNE exclusively involved the [3 + 2] cycloaddition to form **17** and **18** as shown in Table VI. Oxygenation[8] could not be detected even in the polar nitromethane.



(5)

16 **17** **18**

a, X = H, Y = C_6H_5, Z = $CH_2C_6H_5$; **b**, X = C_6H_5, Y = H, Z = $CH_2C_6H_5$; **c**, X = C_6H_5, Y = H, Z = *n*-butyl; **d**, X = C_6H_5, Y = H, Z = Me.

The photoexcitation of the EDA complexes of three-membered compounds such as methylenecyclopropanes, cyclopropanes, and oxiranes with TCNE under aerated conditions thus featured the efficient oxygenations, which strongly depended on the solvent polarity and the electron-donative nature of donor substrates. The photoexcitation, however, is assumed only to facilitate initial electron transfer of EDA complexes to form geminate radical ion pairs. The same reactions were thus expected to occur even in the dark. We found that methylenecyclopropanes **1a–1c** and cyclopropanes **6a–6d** underwent the same reactions in the dark.

$$\textbf{1a–1c} + \text{TCNE} \xrightarrow[\text{dark}]{O_2} \textbf{2a–2c} + \textbf{4a–4c} + \textbf{5a–5c} \qquad (6)$$

$$\textbf{6a–6d} + \text{TCNE} \xrightarrow[\text{dark}]{O_2} \textbf{7a–7d} \qquad (7)$$

When the EDA complexes of **1a–1c** with TCNE were separately stirred in oxygen-saturated dichloromethane at 20 °C for 48 h in the dark, **4** and **5** were obtained together with **2** and **3** as shown in Table VII. Results shown in Tables VII and VIII also show the significant solvent effects on oxygenation in the dark. Similar to the photoexcitation, TMB suppressed oxygenation but anisole did not suppress either oxygenation or the [3 + 2] cycloaddition,[11] as shown in Table VIII. Similarly, **6a–6d** were oxygenated in oxygen-saturated nitromethane upon stirring at 20 °C for 5 h, whereas oxygenation did not occur either in benzene or in dichloromethane, in contrast with the photooxygenation. The yields obtained in the absence or presence of a quencher such as TMB or AN are shown in Table IX.[19] Of these nonphotochemical results, the fact that oxygenation of **1** competed with the [3 + 2] cycloaddition is particularly of interest in connection with the previously proposed mechanism for the thermal cycloaddition reaction of **1d** with TCNE in the dark.[9a] It has been reported that **1d** gave **4d** and **5d** in 35% and 45% yields, respectively, upon heating **1d** with TCNE at 100 °C.[9a] For this cycloaddition, a

Table IX. Yields (%) of Dioxolanes (**7**) from **6** and Effects of Quenchers (TMB and AN) in the Dark[a]

	without TMB		with TMB		with AN	
compd	**7**	con[b]	**7**	con[b]	**7**	con[b]
6a	88	100	87	94	91	100
6b	93	100	28	29	90	100
6c	88	100	10	25	90	100
6d	90	100	0	13	68	100

[a] **6**, TCNE, TMB, AN: 0.10 mmol in 3 mL of nitromethane. [b] Conversion after stirring for 5 h.

Table X. Thermal [3 + 2] Cycloaddition of **1** with TCNE under Nitrogen in Refluxing Toluene

		yield of cycloadducts, %		
compd	reaction time, h	**4**	**5**	con[a]
1a	10	0	84	100
1b	10	24	49	74
	30	8	80	100
1c	10	37	34	72
	30	48	47	100
1d	10	32	24	59
	30	50	36	91
1e	10	16	16	42
	30	35	28	89

[a] Conversion.

$$\textbf{1a–1e} + \text{TCNE} \xrightarrow[\text{under } N_2]{\Delta} \textbf{4a–4e} + \textbf{5a–5e} \qquad (8)$$

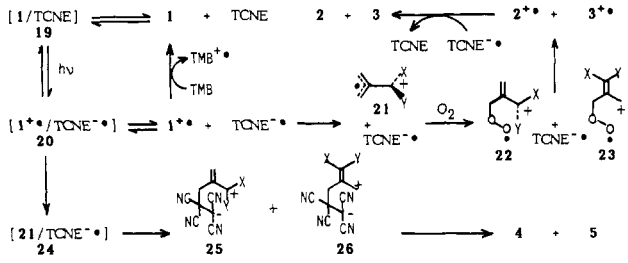
concerted [2 + 2 + 2]-cycloaddition mechanism was proposed, probably because the solvent polarity did not change the disappearance rate of **1d**. The observed product ratio of **4d** and **5d**, however, cannot be explained by a concerted mechanism since TCNE should preferentially approach the less hindered site to form **5d** exclusively. Judging from our photochemical and nonphotochemical results, the only alternative was thus assumed to be an electron-transfer mechanism initiated by the initial EDA interactions. We reexamined the thermal reactions of **1a–1e** with TCNE in refluxing toluene under a nitrogen atmosphere. As shown in Table X, the significant substituent effects on the product ratio and relative disappearance rates of **1** were observed. It was, however, found that the secondary thermal rearrangement of **4** to **5** was important for **1a** and **1b** with relatively low oxidation potentials. Thus, upon heating **4a** quantitatively rearranged to **5a**, and **5b** was exclusively formed upon prolonged heating as shown in Table X. The change in the product ratio, however, was not significant for the less electron donative **1c–1e** even upon prolonged heating. It is thus evident that **4** and **5** are the primary cycloadducts and that **5** does not rearrange to **4**. A decrease in the conversions of **1** with an increase in oxidation potentials also cannot be explained by a concerted mechanism.

Discussion

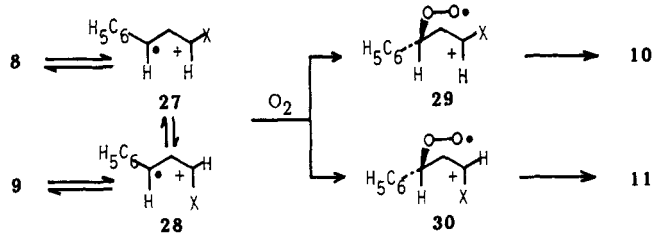
The above photochemical results provided the following general reaction sequences for the photoexcitations of the present EDA complex systems. In general, upon irradiation two mutually independent pathways proceed through the initially formed radical ion pairs [$D^{\bullet+}TCNE^{\bullet-}$]. One is diffusion from [$D^{\bullet+}TCNE^{\bullet-}$] to

(19) The calculated ΔG values for electron transfer from TMB to $6^{\bullet+}$ are −4.4, −5.8, −6.0, and −7.6 kcal/mol, respectively, for **6a–6d** in nitromethane when calculated from the equation $\Delta G = 23.06[E^{ox}_{1/2}(TMB^{\bullet+}/TMB) + E^{ox}_{1/2}(6^{\bullet+}/6) - 0.06]$ kcal/mol.

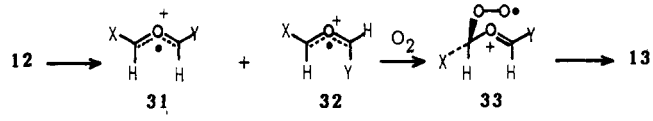
Scheme I



Scheme II



Scheme III



$D^{\bullet+}$ followed by ring cleavage to the ring-opened radical cations $D'^{\bullet+}$, which occurs much more efficiently in the more polar solvents and for the more electron-donative donor substrates. The other is the cage cleavage of $[D^{\bullet+}TCNE^{\bullet-}]$ to $[D'^{\bullet+}TCNE^{\bullet-}]$, which is less sensitive to the solvent polarity. The solvent-assisted former process, and consequent oxygenation, thus exclusively occurs in the polar solvent through $D'^{\bullet+}$. In contrast, the former processes become relatively unfavorable as the solvent polarity decreases, and then the cage cleavage to $[D'^{\bullet+}TCNE^{\bullet-}]$ can compete with the former processes or exclusively occurs to undergo the [3 + 2] cycloaddition by cage coupling. The secondary diffusion from $[D'^{\bullet+}TCNE^{\bullet-}]$ can also generate $D'^{\bullet+}$, competing with the cage coupling, but this process is assumed to be less important as compared with the primary diffusion pathway.

$$D + TCNE \rightleftharpoons [D/TCNE] \overset{h\nu}{\rightleftharpoons} [D^{\bullet+}TCNE^{\bullet-}]$$

$$[D^{\bullet+}TCNE^{\bullet-}] \rightleftharpoons D^{\bullet+} + TCNE^{\bullet-} \rightleftharpoons D'^{\bullet+} + TCNE^{\bullet-}$$

$$D'^{\bullet+} + O_2 \rightarrow \text{di- or trioxolanes}$$

$$[D^{\bullet+}TCNE^{\bullet-}] \rightarrow [D'^{\bullet+}TCNE^{\bullet-}] \rightarrow \text{TCNE-cycloadducts}$$

Among these assertions, one that two reactions occur independently through two different intermediates can be reasonably supported by the following experimental evidences. As observed for **1**, **6**, and **12**, the efficiency of oxygenation dramatically increased as the solvent polarity and the electron-donative nature increased. In contrast, the [3 + 2] cycloaddition was the exclusive pathway in the less polar benzene as observed for **1a** and **12a** and became relatively predominant as the electron-donative nature and the solvent polarity decreased in a series of **1** or **12**. The very efficient and selective oxygenation quenchings by TMB observed for **1** and **12** are strong evidences to support this assertion.

On the basis of this assertion, the photoxygenation and cycloaddition reactions of those donor substrates through EDA complexes can be explained as follows. As a typical case, a plausible mechanism for the EDA complexes of **1** with TCNE is described in Scheme I. As time-resolved spectroscopic studies demonstrated,[4b] the photogenerated radical ion pairs **20**, much more efficiently in the polar solvents, separate into $\mathbf{1}^{\bullet+}$ and $TCNE^{\bullet-}$, competing with the ring cleavage of **20** to **24**. $\mathbf{1}^{\bullet+}$ then successively rearranges to trimethylenemethane cation radicals **21**.[5c] Alternatively, **21** can be generated by the secondary diffusion from **24** which must compete with the low-energy cage coupling to form **25** and **26**. Although the solvent polarity and the electron-donative nature are important equally for both diffusion pathways, those would be primarily more effective for diffusion from **20** since this process is the primary diffusion pathway and the competing cage cleavage of **20** to **24** is less sensitive to the solvent polarity. It would be thus assumed that the primary diffusion from **20** is an exclusive pathway in the polar acetonitrile or nitromethane, at least, for donors with relatively low oxidation potentials such as **1a** and **1b**. Similar argument would be valid for oxiranes such as **12a**, **12b**, and **12d–12f**, in which EDA systems cage coupling could not compete with oxygenation even in dichloromethane. The secondary diffusion, however, cannot be neglected especially in the polar acetonitrile or nitromethane for the less electron-donative donors such as **1c–1e** or in the less polar dichloromethane without regard to oxidation potentials. At this point, the exclusive occurrence of the [3 + 2] cycloaddition in **16** may be suggestive. If the secondary diffusion followed by oxygenation can compete with the cage coupling, oxygenations[8] of **16** should be detected in the polar nitromethane. Results observed for **16** may indicate that the cage coupling of $[D'^{\bullet+}TCNE^{\bullet-}]$ occurs much faster than the secondary diffusion. In the absence of kinetic data, we thus favor major contribution of the primary diffusion pathway for the generation of $D'^{\bullet+}$ in the present EDA-complex systems, though the secondary one cannot be neglected. Electron transfer from TMB to $\mathbf{1}^{\bullet+}$ is highly exothermic as indicated by the calculated ΔG values,[11] whereas those from AN are highly endothermic.[11] Those thermochemical data as well as the fact that the cis–trans isomerizations of **8** and **9** were completely suppressed by TMB indicate that the oxygenation quenchings by TMB are ascribed to the electron-transfer quenching of $\mathbf{1}^{\bullet+}$.

The resulting ring-opened radical cations **21** are then captured by molecular oxygen to form **22** and **23**. The successive bond formations followed by back-electron-transfer from $TCNE^{\bullet-}$ generate **2** and **3** together with TCNE. The regenerated TCNE then re-enters the EDA complex formation cycle. The observations that the amounts of TCNE did not affect oxygenations of **6** and **12** well indicate the catalyst-like role of TCNE for oxygenation. Since oxygenations of **1** and **6** occurred even in the dark and electron, transfer from $TCNE^{\bullet-}$ to triplet oxygen is highly endothermic (+30.9 kcal/mol in dichloromethane) so that the formation of oxygen anion radical cannot be expected,[20] the reactions of ring-opened radical cations with triplet molecular oxygen should be taken into account for oxygenations of **1** and **6** as well as highly stereoselective oxygenations of **8**, **9**, and **12**. Evidences that oxygenations of **1a–1c** and **6a–6e** were also catalyzed by tris(*p*-bromophenyl)aminium hexachloroantimonate[22] in the dark can be taken as further evidence in support of this assertion. The highly stereoselective oxygenations **8**, **9**, and **12** can be explained by a two-step addition mechanism shown in Scheme II and III. The photostationary cis–trans isomerization occurs through radical cations **27** and **28** in favor of the formation of **9**. Addition of triplet oxygen with **27** and **28** generates peroxy radical cations **29** and **30**. The less sterically hindered **29** gives the cis isomer **10** as a major product. This mechanism does not require the retention of the cis–trans isomerization ratio in the oxygenation step. Similarly, the stereoselective formation of **13** can be explained as follow. Judging from previously reported photosensitized electron-transfer reactions of oxiranes,[23] the ring cleavage of $\mathbf{12}^{\bullet+}$ should occur nonstereoselectively to form (*E*,*E*) and (*E*,*Z*) radical cations **31** and **32** which, in turn, are intercepted by triplet oxygen

(20) Calculated from the equation $\Delta G = 23.06[E^{red}_{1/2}(TCNE) - E^{red}_{1/2}(O_2) + 0.16]$ kcal/mol, where $E^{red}_{1/2}(TCNE) = +0.24$ V vs. SCE and $E^{red}_{1/2}(O_2) = -0.94$ V vs. SCE. Cyclic voltammetric analyses of TCNE in the presence or absence of oxygen by Tokumaru and Akaba[21] also support this assertion.

(21) Akaba, R.; Sakuragi, H.; Tokumaru, K. *Chem. Lett.* **1984**, 1677.

(22) Barton, D. H. R.; Leclerc, G.; Magnus, P. D.; Menzies, I. D. *J. Chem. Soc., Chem. Commun.* **1972**, 447. Tang, R.; Yue, H. J.; Wolf, J. F.; Mares, F. *J. Am. Chem. Soc.* **1978**, *100*, 5248.

(23) (a) Albini, A.; Arnold, D. R. *Can. J. Chem.* **1978**, *56*, 2985. (b) Wong, J. P. K.; Fahmi, A. A.; Griffin, G. W.; Bhacca, N. S. *Tetrahedron* **1981**, *37*, 3345. (c) Clawson, P.; Lunn, P. M.; Whiting, D. A. *J. Chem. Soc., Chem. Commun.* **1984**, 134.

to give peroxy radical cations. Because of the low rotational barrier around the C—O$^+$=C bond, the second C—O bond formation occurs exclusively through the least hindered **33** to form *cis*-**13**. The fact that the same stereoselective photooxygenations as those observed under DCA-sensitized conditions nevertheless took place under conditions[24] in which neither oxygen anion radical nor singlet oxygen is generated, thus, strongly indicates that singlet oxygen might not be necessarily responsible for the stereoselective oxygenation of oxiranes under DCA-sensitized conditions.[7c,d] This fact rather suggests that the responsibility of triplet oxygen for the electron-transfer oxygenation cannot be simply precluded even under DCA-sensitized conditions.[26]

On the other hand, the [3 + 2] cycloaddition of **1** with TCNE rapidly occurs by coupling of radical ion pairs **24** generated from **20**, giving **25** and **26**. The observed insensibilities of the [3 + 2] cycloaddition to the solvent polarity and the reaction quenching by TMB in both photochemical and thermal[9a] processes are evidence that the [3 + 2] cycloaddition is initiated by the rate-determining cage cleavage of **20**. Thus, the essentially same electron-transfer mechanism can be proposed for the thermal [3 + 2]-cycloaddition reaction of **1** with TCNE. At room temperature, the [3 + 2] cycloaddition occurs in the same mechanism as the photochemical one shown in Scheme I. The irreversible secondary thermal processes between **4** and **5**, however, must be taken into account for the [3 + 2] cycloaddition at high temperature for donors such as **1a** and **1b** with relatively low oxidation potentials. Similarly, the [3 + 2] cycloadditions of **12** and **16**

$$4 \overset{\Delta}{\rightleftharpoons} 25 \rightleftharpoons 26 \rightarrow 5 \qquad (9)$$

can be explained either by rapid coupling of ring-opened radical ion pairs [D$'^{\bullet+}$TCNE$^{\bullet-}$] or more likely by an alternative concerted addition of carbonyl ylides and azomethine ylides with TCNE, respectively, which could be generated after back-electron-transfer of [D$'^{\bullet+}$TCNE$^{\bullet-}$].[23a] The observed solvent effects and efficient oxygenation quenchings by TMB also suggest that the [3 + 2] cycloaddition occurred through radical ion pairs but not through diffused ring-opened radical cations.

One additional intriguing feature observed is that the general trend in the efficiency of oxygenation obviously varied in the order **6** > **12** > **1**, whereas that of [3 + 2] cycloaddition increased in the reverse order **16** > **1** > **12**. Those efficiencies seem to increase with a decrease and an increase in oxidation potentials, respectively, at least if the reactivities of donor substrates with the lowest oxidation potential in each donor system are compared. For **6a** with relatively low oxidation potentials, diffusion to D$^{\bullet+}$ might overcome the cage cleavage to [D$'^{\bullet+}$TCNE$^{\bullet-}$], while the later process might overcome the former process in the photoexcitation of the EDA complexes of **16a** with relatively high oxidation potentials. Intermediately electron donative **1a** and **12a** underwent both reactions, significantly depending on the solvent polarity. Such an explanation based on the effects of oxidation potentials is valid enough to explain the orders of efficiencies within each donor system but most sufficient enough to explain whole results including those orders over all donor systems. For instance, it is not easy to explain reasonably why the [3 + 2] cycloaddition is the exclusive pathway for **16**, which is of comparable electron donativity as compared with **1c–1e** and **12f–12h**, and also why cyclopropanes did not undergo the [3 + 2] cycloaddition. Since **1**, **12**, and **16**, which gave stable ring-opened trimethylenemethane, carbonyl ylide, and azomethine ylide radical cations, respectively, all undergo the [3 + 2] cycloaddition and the order **16** > **1** > **12** also seems to accord with the order of the thermolabile nature, the stability of D$'^{\bullet+}$ may be important for the [3 + 2] cycloaddition. It should also be considered for those points that effects of the solvent polarity and the oxidation potential may play differently in each donor system. Nevertheless, the present study experimentally proved that two different radical ion intermediates generate from the photogenerated radical ion pair and behave differently under aerated conditions.

Experimental Section

General. All melting and boiling points are uncorrected. Elemental analyses were performed by the Instrumental Analyses Center for Chemistry, Faculty of Science, Tohoku University. IR and UV spectra were recorded on a Shimadzu IR-435 and a Carry 219 spectrometer, respectively. Mass data were collected on a Hitachi M-52 mass spectrometer. ^{1}H NMR spectra were obtained at 90 MHz on a Varian EM-390 spectrometer. Chemical shifts were reported by using the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad; *J*, coupling constant (hertz). Half-wave oxidation potentials were measured on a Yanaco P-1000 voltammetric analyzer by cyclic voltammetry. Tetracyanoethylene was purified by repeated sublimation. Dichloromethane and acetonitrile were each distilled over calcium hydride prior to use. Benzene was distilled over sodium wires. Spectroscopic grade nitromethane was used as solvent. Preparative thick-layer chromatography (TLC) was performed on 0.5-mm × 20-cm × 20-cm silica gel (E. Merck $60PF_{254}$) plates.

Syntheses, Oxidation Potentials of 1, 6, 12, and 16, and the Charge-Transfer Absorptions of the EDA Complexes with TCNE. 1a–1e,[28] **6a–6f,**[29] **12a–12h,**[30] and **16a–16d**[31] were prepared according to reported procedures. The oxidation potentials shown in Table I were measured by cyclic voltammetry at a platinum electrode with 0.1 M tetraethylammonium perchlorate as a supporting electrolyte in dry acetonitrile. The charge-transfer absorptions shown in Table I were measured soon after mixing **1**, **6**, **12**, and **16** (5.0×10^{-2} M) with TCNE (5.0×10^{-2} M) in dry dichloromethane.

Irradiations of the EDA Complexes of 1, 6, 12, and 16 with TCNE under Oxygen or Nitrogen. In general, a solution of each donor (0.10 mmol) and TCNE (0.02 or 0.10 mmol) in 3 mL of oxygen- or nitrogen-saturated benzene, dichloromethane, nitromethane, or acetonitrile was placed in a 10-mL Pyrex tube and maintained at 15–20 °C in a water-filled Pyrex Dewar. The solution was irradiated with light from a 2-kW xenon lamp through a Toshiba glass cutoff filter L-42 (390 nm). The solvent was evaporated, and the resulting residue was taken into $CDCl_3$ and subject to ^{1}H NMR analysis using *tert*-butylbenzene or diphenylmethane as an internal standard. Among the products, **2a**,[5a] **2c–2e**,[5a] **4d**,[9a] **5d**,[9a] **13a–13c**,[7h] and **13h**[7c] are known and independently synthesized according to the reported procedures and isolated by TLC. Dioxolanes **7a–7f**, **10**, and **11**, and trioxolanes **13a–13g** were independently synthesized under the DCA-sensitized conditions in oxygen-saturated acetonitrile. *cis*-Trioxolane **13h** was synthesized by DCA–biphenyl-cosensitized irradiation.[7c] Those trioxolanes and dioxolanes isolated in this report were proved to be identical with those synthesized under the DCA-sensitized conditions by comparisons of their IR and ^{1}H NMR spectra and the mixed melting point determination. The melting points, mass, and ^{1}H NMR spectra of all new compounds are described

(24) Since oxygen anion radical is not generated under the present irradiation conditions,[20] the generation of singlet oxygen by back-electron-transfer from the ring-opened radical cations of **12** to oxygen anion radical[7c,d] is highly unfeasible. Under the present irradiation conditions, singlet oxygen could be alternatively generated by energy transfer from triplet oxirane (or TCNE) to triplet oxygen if such a species can be generated by back-electron-transfer in radical ion pairs or by energy transfer from initially formed excited EDA complexes to oxygen, if such excited species are sufficiently long-lived. Back-electron-transfer in radical ion pairs can generate neither triplet oxirane nor TCNE since their triplet energies are much higher than the energies stored in the radical ion pairs which, for instance, are calculated to be 23.8, 27.2, 28.4, 28.4, 28.6, 29.7, 31.6, and 36.4 kcal/mol, respectively, for **12a–12h**. Sensitization by excited EDA complexes is also highly unlikely since such excited species are generally very short-lived and are rapidly converted into radical ion pairs.[4] Indirect evidence which indicates the improbability of generating singlet oxygen under the present conditions is that TMB, used as a quencher and known to be labile to singlet oxygen,[25] remained unchanged and was recovered quantitatively.

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below. IR spectra were not described.

2b: oil; MS, *m/e* (relative intensity) 268 (M^+, 38), 210 (100), 135 (94), 105 (65); ^1H NMR ($CDCl_3$), δ 3.78 (3 H, s), 4.87 (1 H, m), 5.29 (1 H, m), 6.75–7.50 (9 H, m).

Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 75.65; H, 6.11.

4a: not isolated. **4a** readily isomerized to **5a** on a silica gel TLC plate: ^1H NMR ($CDCl_3$) δ 3.70 (2 H, m), 3.75 (6 H, s), 5.49 (1 H, m), 5.70 (m, 1 H), 6.80–7.10 (4 H, m), 7.20–7.50 (4 H, m).

5a: mp 152 °C; MS, *m/e* (relative intensity) 394 (M^+, 67), 266 (100), 191 (37); ^1H NMR ($CDCl_3$) δ 3.51 (4 H, s), 3.72 (6 H, s), 6.75–7.20 (8 H, m).

Anal. Calcd for $C_{24}H_{18}O_2N_4$: C, 73.08; H, 4.60; N, 14.21. Found: C, 72.67; H, 4.37; N, 14.08.

4b: mp 146 °C; MS, *m/e* (relative intensity) 364 (M^+, 58), 221 (40), 205 (35); ^1H NMR ($CDCl_3$) 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 (m, 7 H).

Anal. Calcd for $C_{23}H_{16}N_4O$: C, 75.81; H, 4.43; N, 15.38. Found: C, 75.61; H, 4.33; N, 15.28.

5b: mp 125 °C; MS, *m/e* (relative intensity) 364 (M^+, 63), 236 (100), 221 (37), 205 (24); ^1H NMR ($CDCl_3$) δ 3.48 (2 H, s), 3.54 (2 H, s), 3.80 (3 H, s), 6.70–7.60 (9 H, m).

Anal. Calcd for $C_{23}H_{16}N_4O$: C, 75.81; H, 4.43; N, 15.38. Found: C, 75.77; H, 4.35; N, 15.30.

4c: mp 181 °C; MS, *m/e* (relative intensity) 362 (M^+, 24), 234 (74), 219 (100); ^1H NMR ($CDCl_3$) 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).

Anal. Calcd for $C_{24}H_{18}N_4$: C, 79.53; H, 5.01; N, 15.46. Found: C, 79.42; H, 4.86; N, 15.40.

5c: mp 170 °C; MS, *m/e* (relative intensity) 362 (M^+, 31), 234 (48), 219 (100); ^1H NMR ($CDCl_3$) δ 2.34 (6 H, s), 3.50 (4 H, s), 6.95–7.25 (8 H, m).

Anal. Calcd for $C_{24}H_{18}N_4$: C, 79.53; H, 5.01; N, 15.46. Found: C, 79.43; H, 4.97; N, 15.56.

4e: mp 196 °C; MS, *m/e* (relative intensity) 403 (M^+, 14), 239 (100), 204 (56); ^1H NMR ($CDCl_3$) δ 3.73 (2 H, m), 5.51 (1 H, m), 5.79 (1 H, m), 7.20–7.53 (8 H, m).

Anal. Calcd for $C_{22}H_{22}N_4Cl_2$: C, 65.52; H, 3.00; N, 13.90; Cl, 17.58. Found: C, 65.60; H, 2.92; N, 13.99; Cl, 17.51.

5e: mp 164 °C, MS, *m/e* (relative intensity) 403 (M^+, 72), 239 (100), 204 (60); ^1H NMR ($CDCl_3$) δ 3.50 (4 H, s), 6.90–7.23 (4 H, m), 7.25–7.55 (4 H, m).

Anal. Calcd for $C_{22}H_{22}N_4Cl_2$: C, 65.52; H, 3.00; N, 13.90; Cl, 17.58. Found: C, 65.81; H, 2.82; N, 14.06; Cl, 17.49.

7a: mp 106 °C; MS, *m/e* (relative intensity) 438 (M^+, 5), 406 (17), 135 (100), 105 (64); ^1H NMR ($CDCl_3$) δ 3.76 (6 H, s), 4.04 (2 H, s), 6.67–7.47 (18 H, m).

Anal. Calcd for $C_{29}H_{26}O_4$: C, 79.43; H, 5.98. Found: C, 79.68; H, 6.18.

7b: mp 110 °C; MS, *m/e* (relative intensity) 422 (M^+, 8), 390 (22), 105 (100); ^1H NMR ($CDCl_3$) δ 2.30 (3 H, s), 3.75 (3 H, s), 4.05 (2 H, s), 6.65–7.56 (18 H, m).

Anal. Calcd for $C_{29}H_{26}O_3$: C, 82.44; H, 6.20. Found: C, 82.65; H, 6.10.

7c: mp 142 °C; MS, *m/e* (relative intensity) 408 (M^+, 7), 376 (17), 212 (41), 182 (52), 135 (91), 105 (100); ^1H NMR ($CDCl_3$) δ 3.77 (3 H, s), 4.10 (2 H, s), 6.63–7.53 (19 H, m).

Anal. Calcd for $C_{28}H_{24}O_3$: C, 82.33; H, 5.92. Found: C, 82.41; H, 6.03.

7d: mp 94 °C; MS, *m/e* (relative intensity) 442 (M^+, 6), 410 (17), 246 (34), 182 (31), 135 (100); ^1H NMR ($CDCl_3$) δ 3.72 (3 H, s), 3.97 (1 H, d, J = 13 Hz), 4.10 (1 H, d, J = 13 Hz), 6.65–7.57 (18 H, m).

Anal. Calcd for $C_{28}H_{23}O_3Cl$: C, 75.93; H, 5.23; Cl, 8.00. Found: C, 76.40; H, 5.40; Cl, 8.20.

7e: mp 128 °C; MS, *m/e* (relative intensity) 406 (M^+, 8), 374 (25), 210 (34), 195 (45), 182 (45), 119 (84), 105 (100); ^1H NMR ($CDCl_3$) δ 2.30 (6 H, s), 4.06 (2 H, s), 6.90–7.47 (18 H, m).

Anal. Calcd for $C_{29}H_{26}O_2$: C, 85.68; H, 6.45. Found: C, 85.52; H, 6.45.

13d: mp 84–85 °C; MS, *m/e* (relative intensity) 292 (M^+, 1), 136 (100), 260 (1); ^1H NMR ($CDCl_3$) δ 3.82 (3 H, s), 6.23 (1 H, s), 6.31 (1 H, s), 6.81–7.04 (2 H, m), 7.28–7.61 (7 H, m).

Anal. Calcd for $C_{15}H_{13}O_4Cl$: C, 61.55; H, 4.48; Cl, 12.11. Found: C, 61.45; H, 4.73; Cl, 12.17.

13f: mp 64–65 °C; MS, *m/e* (relative intensity) 303 (M^+, 3), 271 (9), 151 (100); ^1H NMR ($CDCl_3$) δ 3.80 (3 H, s), 6.20 (1 H, s), 6.45 (1 H, s), 6.77–7.07 (2 H, m), 7.20–7.45 (2 H, m), 7.60–7.90 (2 H, m), 8.13–8.40 (2 H, m).

Anal. Calcd for $C_{15}H_{13}NO_6$: C, 59.40; H, 4.32; N, 4.62. Found: C, 59.29; H, 4.21; N, 4.61.

13g: mp 126 °C; MS, *m/e* (relative intensity) 256 (M^+, 3), 224 (9), 120 (100); ^1H NMR ($CDCl_3$) δ 2.37 (6 H, s), 6.27 (2 H, s), 7.09–7.32 (4 H, m), 7.32–7.52 (4 H, m).

Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.36; H, 6.42.

14a: mp 198 °C; MS, *m/e* (relative intensity) 384 (M^+, 1), 136 (100); ^1H NMR ($CDCl_3$) δ 3.88 (6 H, s), 5.52 (2 H, s), 6.95–7.20 (4 H, m), 7.43–7.70 (4 H, m).

Anal. Calcd for $C_{22}H_{16}N_4O_3$: C, 68.74; H, 4.20; N, 14.58. Found: C, 68.59; H, 4.12; N, 14.49.

15a: mp 156 °C; MS, *m/e* (relative intensity) 384 (M^+, 7), 256 (51), 136 (100); ^1H NMR ($CDCl_3$) δ 3.86 (6 H, s), 5.91 (2 H, s), 6.90–7.20 (4 H, m), 7.38–7.65 (4 H, m).

Anal. Calcd for $C_{22}H_{16}N_4O_3$: C, 68.74; H, 4.20; N, 14.58. Found: C, 69.03; H, 4.04; N, 14.49.

14b: mp 200 °C; MS, *m/e* (relative intensity) 368 (M^+, 3), 240 (100); ^1H NMR ($CDCl_3$) δ 2.44 (3 H, s), 3.87 (3 H, s), 5.52 (2 H, s), 6.90–7.70 (8 H, m).

Anal. Calcd for $C_{22}H_{16}N_4O_2$: C, 71.72; H, 4.38; N, 15.21. Found: C, 71.86; H, 4.35; N, 15.

15b: mp 159 °C; MS, *m/e* (relative intensity) 368 (M^+, 12), 240 (100); ^1H NMR ($CDCl_3$) δ 2.42 (3 H, s), 3.86 (3 H, s), 5.91 (1 H, s), 5.93 (1 H, s), 6.90–7.76 (8 H, m).

Anal. Calcd for $C_{22}H_{16}N_4O_2$: C, 71.72; H, 4.38; N, 15.21. Found: C, 70.78; H, 4.26; N, 14.72.

14c: mp 187 °C; MS, *m/e* (relative intensity) 354 (M^+, 1), 226 (100); ^1H NMR ($CDCl_3$) δ 3.87 (3 H, s), 5.55 (2 H, s), 6.98–7.17 (2 H, m), 7.45–7.67 (7 H, m).

Anal. Calcd for $C_{21}H_{14}N_4O_2$: C, 71.18; H, 3.98; N, 15.81. Found: C, 70.55; H, 3.71; N, 15.42.

15c: mp 124 °C; MS, *m/e* (relative intensity) 354 (M^+, 1), 226 (1), 128 (100); ^1H NMR ($CDCl_3$) δ 3.88 (3 H, s), 5.94 (1 H, s), 5.98 (1 H, s), 6.97–7.20 (2 H, m), 7.47–7.77 (7 H, m).

Anal. Calcd for $C_{21}H_{14}N_4O_2$: C, 71.18; H, 3.98; N, 15.81. Found: C, 71.32; H, 3.79; N, 15.82.

14d: mp 210 °C; MS, *m/e* (relative intensity) 388 (M^+, 1), 260 (100); ^1H NMR ($CDCl_3$) δ 3.86 (3 H, s), 5.52 (1 H, s), 5.55 (1 H, s), 6.93–7.20 (2 H, m), 7.45–7.70 (6 H, m).

Anal. Calcd for $C_{21}H_{13}N_4O_2Cl$: C, 64.87; H, 3.37; N, 14.41. Found: C, 64.96; H, 3.12; N, 14.55.

15d: mp 158 °C; MS, *m/e* (relative intensity) 388 (M^+, 1), 260 (100); ^1H NMR ($CDCl_3$) δ 3.86 (3 H, s), 5.92 (1 H, s), 5.94 (1 H, s), 6.90–7.20 (2 H, m), 7.35–7.67 (6 H, m).

Anal. Calcd for $C_{21}H_{13}N_4O_2Cl$: C, 64.87; H, 3.37; N, 14.41. Found: C, 64.96; H, 3.12; N, 14.40.

14g: mp 244 °C; MS, *m/e* (relative intensity) 352 (M^+, 1), 224 (100), 120 (67); ^1H NMR ($CDCl_3$) δ 2.44 (6 H, s), 5.53 (2 H, s), 7.23–7.67 (8 H, m).

Anal. Calcd for $C_{22}H_{16}N_4O$: C, 74.98; H, 4.58; N, 15.90. Found: C, 74.92; H, 4.36; N, 15.81.

15g: mp 164–165 °C; MS, *m/e* (relative intensity) 352 (M^+, 5), 224 (100), 120 (44); ^1H NMR ($CDCl_3$) δ 2.43 (6 H, s), 5.93 (2 H, s), 7.20–7.60 (8 H, m).

Anal. Calcd for $C_{22}H_{16}N_4O$: C, 74.98; H, 4.58; N, 15.90. Found: C, 75.19; H, 4.35; N, 15.94.

14h: mp 223–224 °C; MS, *m/e* (relative intensity) 324 (M^+, 1), 196 (100); ^1H NMR ($CDCl_3$) δ 5.65 (2 H, s), 7.45–7.85 (10 H, m).

Anal. Calcd for $C_{20}H_{12}N_4O$: C, 74.06; H, 3.73; N, 17.28. Found: C, 74.18; H, 3.62; N, 17.21.

15h: mp 166 °C; MS, *m/e* (relative intensity) 324 (M^+, 1), 196 (100); ^1H NMR ($CDCl_3$) δ 6.03 (2 H, s), 7.45–7.77 (10 H, m).

Anal. Calcd for $C_{20}H_{12}N_4O$: C, 74.06; H, 3.73; N, 17.28. Found: C, 74.01; H, 3.61; N, 17.23.

17a: mp 195 °C; MS, *m/e* (relative intensity) 413 (M^+, 2), 322 (6), 285 (11), 194 (100), 92 (19); ^1H NMR ($CDCl_3$) δ 3.85 (2 H, s), 4.40 (2 H, s), 6.60–6.90 (2 H, m), 7.15–7.45 (3 H, m), 7.45–7.90 (10 H, m).

Anal. Calcd for $C_{31}H_{19}N_5$: C, 78.43; H, 4.63; N, 16.94. Found: C, 78.68; H, 4.47; N, 16.69.

18a: ^1H NMR ($CDCl_3$) δ 3.57 (1 H, d, J = 14 Hz), 3.98 (1 H, d, J = 14 Hz), 5.20 (2 H, s), 6.60–7.90 (15 H, m).

17c: mp 135–136 °C; MS, *m/e* (relative intensity) 379 (M^+, 6), 336 (67), 251 (100), 207 (58), 194 (42), 174 (23), 116 (27); ^1H NMR ($CDCl_3$) δ 0.47–0.77 (3 H, s), 0.77–1.42 (4 H, m), 2.47–2.85 (2 H, m), 4.63 (2 H, m), 7.30–7.87 (10 H, m).

Anal. Calcd for $C_{24}H_{21}N_5$: C, 75.96; H, 5.58; N, 18.46. Found: C, 75.99; H, 5.80; N, 18.44.

18c: ^1H NMR ($CDCl_3$) δ 0.47–0.77 (3 H, m), 0.77–1.42 (4 H, m), 2.47–2.85 (2 H, m), 5.27 (2 H, s), 7.50 (10 H, br s).

17d: mp 243 °C; MS, *m/e* (relative intensity) 337 (M^+, 2), 209 (90), 208 (100), 194 (21); ^1H NMR ($CDCl_3$) δ 2.28 (3 H, s), 4.31 (2 H, s), 7.40-7.80 (10 H, m).

Anal. Calcd for $C_{21}H_{15}N_5$: C, 74.76; H, 4.48; N, 20.76. Found: C, 75.14; H, 4.61; N, 20.83.

18d: ^1H NMR ($CDCl_3$) δ 2.31 (3 H, s), 5.22 (2 H, s), 7.40-7.80 (10 H, m).

Oxygenations and the [3 + 2] Cycloadditions of 1 and 6 in the Dark. The same oxygen-saturated solution exactly as described for the irradiation was stirred in the dark at room temperature. **1d** and **1e** were not oxygenated in acetonitrile and quantitatively recovered.

Tris(*p*-bromophenyl)aminium Hexachloroantimonate Catalyzed Oxygenations of 1a-1c and 6a-6e. A solution of **1** or **6** (0.1 mmol) and antimonate (0.025 mmol) in 3 mL of oxygen-saturated nitromethane was stirred at room temperature in the dark. **2a**, **2b**, and **2c** were isolated in 49%, 26%, and 71% yields, respectively, after 2 h of stirring. **7a-7e** were similarly isolated in 91%, 88%, 77%, 91%, and 22% yields, respectively, after 5 h of stirring in the dark.

Quenching Experiments. A solution of EDA complex with TCNE was irradiated or stirred in the dark in the presence of a quencher such as TMB or AN as described before. Neither cis-trans isomerization nor oxygenation of **8** was observed when a solution of **8** (0.10 mmol), TCNE (0.10 mmol), and TMB (0.10 mmol) in oxygen-saturated dichloromethane or nitromethane (3 mL) was irradiated for 3 h.

Thermal [3 + 2] Cycloadditions of 1 with TCNE. A solution of **1** (0.10 mmol) and TCNE (0.12 mmol) in 10 mL of dry toluene was heated under reflux in a nitrogen atmosphere.

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Registry No. 1a·TCNE, 107245-62-5; **1b**·TCNE, 107245-63-6; **1c**·TCNE, 107245-64-7; **1d**·TCNE, 107245-65-8; **1e**·TCNE, 107245-66-9; **2b**, 101810-64-4; **4a**, 107245-87-4; **4b**, 101810-66-6; **4c**, 101810-67-7; **4e**, 107245-88-5; **5a**, 101810-68-8; **5b**, 101810-69-9; **5c**, 101810-70-2; **5e**, 107245-89-6; **6a**·TCNE, 107245-67-0; **6b**-TCNE, 107245-69-2; **6c**·TCNE, 107245-70-5; **6d**·TCNE, 107269-61-4; **6e**·TCNE, 107245-72-7; **6f**·TCNE, 107245-73-8; **7a**, 107245-90-9; **7b**, 107299-76-3; **7c**, 107245-91-0; **7d**, 107245-92-1; **7e**, 107245-93-2; *trans*-**12a**·TCNE, 107245-74-9; *trans*-**12b**·TCNE, 107245-75-0; *cis*-**12c**·TCNE, 107245-76-1; *trans*-**12d**·TCNE, 107245-78-3; *trans*-**12e**·TCNE, 107245-79-4; *trans*-**12f**·TCNE, 107245-80-7; *trans*-**12g**·TCNE, 107245-81-8; *trans*-**12h**·TCNE, 107245-82-9; **13d**, 107245-94-3; **13f**, 107245-95-4; **13g**, 107245-96-5; **14a**, 107245-97-6; **14b**, 107245-99-8; **14c**, 107246-01-5; **14d**, 107246-03-7; **14g**, 107246-09-3; **14h**, 107246-11-7; **15a**, 107245-98-7; **15b**, 107246-00-4; **15c**, 107246-02-6; **15d**, 107246-08-2; **15g**, 107246-10-6; **15h**, 107246-12-8; *trans*-**16a**·TCNE, 107245-83-0; *cis*-**16b**·TCNE, 107245-84-1; *cis*-**16c**·TCNE, 107245-85-2; *cis*-**16d**·TCNE, 107245-86-3; **17a**, 107246-13-9; **17c**, 107246-05-9; **17d**, 107246-06-0; **18a**, 107246-04-8; **18c**, 107269-62-5; **18d**, 107246-07-1; tris(*p*-bromophenyl)aminium hexachloroantimonate, 40927-19-3; TMB, 95-93-2.

Cyclization of Diacetylenes to *E,E* Exocyclic Dienes. Complementary Procedures Based on Titanium and Zirconium Reagents†

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Abstract: The intramolecular cyclization of diacetylenes has been achieved by using either of the reagent combinations $Cp_2TiCl_2/PMePh_2/Na(Hg)$ or $Cp_2ZrCl_2/Mg/HgCl_2$ in solvent tetrahydrofuran. The procedures are compatible with a variety of saturated functionality (O, N, Si), and in each case, acid hydrolysis of the initially formed organometallic intermediate affords exclusively the *E,E* exocyclic diene. For synthesis of simple five- and six-membered-ring dienes, especially on a multigram scale, the titanium procedure is superior. The zirconium procedure is preferred for preparation of dienes containing bulky substituents or a four- or seven-membered ring. The mechanism of these transformations has been probed by extended Hückel molecular orbital calculations and X-ray crystal structures of the metallacyclic intermediates. The extreme facility of the cyclization is traced to the electronic structure of the intermediate d^2 acetylene complexes.

The selective formation of carbon-carbon bonds is frequently the most demanding step in organic synthesis. It is therefore not surprising that there is intense current interest in the development of new methodology in which the selectivity of C-C bond formation is controlled by a transition-metal template.[1] Although there are important exceptions, the substrates for such transition-metal-mediated reactions are typically organic molecules containing carbon-carbon unsaturations (e.g., alkenes, alkynes, arenes) rather than the carbonyl derivatives which serve as the basic building blocks of conventional synthesis. This represents both an advantage and a disadvantage to the synthesis chemist: On the one hand, such molecules (especially acetylenes) are readily prepared by simple, high-yield reactions. They are stable toward many reaction conditions (base, nucleophiles, reductions) required to assemble other portions of a complex organic molecule. On the other hand, with such molecules lacking the intrinsic polarization of carbonyl derivatives, the control of regiochemistry can be problematic.

This difficulty applies to the "oxidative coupling" reaction (eq 1) which has been observed by several workers[2] upon treating diphenylacetylene with various titanocene or zirconocene precursors. Notable among these procedures in terms of operational simplicity is that of Farona[2a] in which the source of the zirconocene equivalent consists of a mixture of commercially available bis(cyclopentadienyl)zirconium dichloride and magnesium turnings.[3] Cleaving the resultant metallacycle with acid releases exclusively

† Dedicated to Professor J. K. Kochi on the occasion of his 60th birthday.

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(3) Another convenient zirconocene source for cyclic carbometallation reactions has recently been described: Negishi, E.; Cederbaum, F. E.; Tamotsu, T. *Tetrahedron Lett.* **1986**, *27*, 2829-2832.

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