Stereoselective Oxygenation of 2,3-Diaryloxiranes by Irradiation of Electron Donor–Acceptor Complexes of Tetracyanoethylene

Tsutomu Miyashi,* Masaki Kamata, and Toshio Mukai

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

On irradiation of the electron donor–acceptor complexes of 2,3-diaryloxiranes with tetracyanoethylene (TCNE) in the presence of oxygen, *cis*-trioxolanes are formed stereoselectively; a nonstereoselective [3 + 2]cycloaddition with TCNE competes with trioxolane formation.

On irradiation of electron donor–acceptor (EDA) complexes of methylenecyclopropane (MCP) with tetracyanoethylene (TCNE) under oxygen,[1] we have demonstrated that oxygenation to form dioxolanes takes place through MCP radical ions which have diffused from photogenerated geminate radical ion pairs [MCP$^{\cdot+}$, TCNE$^{\cdot-}$], whereas [3 + 2]cycloaddition with TCNE occurs *via* [MCP$^{\cdot+}$, TCNE$^{\cdot-}$] as a cage process.

In studying the title reactions we hoped to obtain confirmation of these general reaction sequences initiated by photoexcitation of EDA complexes,[1,2] and to gain insight into the mechanisms proposed by Ohta[3] and Schaap[4] for photoinduced electron-transfer oxygenations of oxiranes. Schaap *et al.* have concluded that the 9,10-dicyanoanthracene (DCA)-sensitised photo-oxygenations of *cis*- and *trans*-2,3-diphenyloxiranes stereoselectively gave *cis*-trioxolane.[4] The key mechanistic step to account for the stereoselectivity was proposed to be a concerted addition of an (*E*,*E*)-carbonyl ylide to singlet oxygen, both of which are assumed to be generated by a second electron-transfer step from the oxygen anion radical to the ring-opened radical cations of 2,3-diphenyloxiranes.[4] However, why a second electron-transfer occurs instead of the usual C–O bond formation is unclear. Also there is no evidence which rules out the possibility that triplet oxygen captures the ring-opened radical cations.[1] Therefore it is of interest to establish whether triplet oxygen is responsible for the stereoselective oxygenation of oxiranes or not. Oxygenation of oxiranes *via* EDA complexes seems suitable to test this possibility since neither singlet oxygen nor an oxygen radical anion can be generated under the oxygenation conditions.†

cis- and *trans*-2,3-Diaryloxiranes (**1**) form coloured EDA complexes when mixed with TCNE in dry dichloromethane. Upon irradiation (>390 nm) of the EDA complex of TCNE–(**1a**) (0.1 mmol each) in dichloromethane (3 ml) under nitrogen for 1 h, [3 + 2]cycloadducts (**3a**) (m.p. 197—198 °C)‡ and (**4a**) (m.p. 155—156 °C)‡ were afforded in 27 and 26% yields, respectively, whereas under oxygen *cis*-trioxolane (**2a**) (m.p. 76—78 °C)[3] was obtained in 87% yield as the sole product. Under the same oxygenation conditions, (**2c**) (m.p. 84—85 °C)‡ and (**2d**) (m.p. 63—65 °C)‡ were isolated, respectively, from (**1c**) and (**1d**). *cis*- and *trans*-Oxiranes (**1b**) and (**1d**) gave the same trioxolane§[3] together with (**3b**) (m.p. 186—187 °C)‡ and (**4b**) (m.p. 122—124 °C).‡ Oxirane (**1e**)§ with a relatively high oxidation potential similarly afforded both trioxolane (**2e**) (m.p. 98—100 °C)[4] and [3 + 2]cycloadducts (**3e**) (m.p. 223—224 °C)‡ and (**4e**) (m.p. 165—166 °C).‡

Trioxolanes (**2a**—**e**) proved to be identical with those independently isolated under dicyanoanthracene (DCA)-sensitised[3] or DCA–biphenyl cosensitised[4] conditions, confirming the *cis*-stereochemical assignment.[4]

Interesting features of this study are: (i) the amounts of TCNE do not significantly change the yields of oxygenation products, indicating that TCNE is regenerated in the oxygenation cycle. (ii) Addition of 1,2,4,5-tetramethoxybenzene (TMB) as a quencher completely suppressed oxygenation but did not affect [3 + 2]cycloaddition with TCNE.¶ (iii) The solvent polarity could control the reaction pathway. Thus, in non-polar benzene (**1a**) gave (**3a**) (28%) and (**4a**) (25%) together with a trace of (**2a**), while in polar acetonitrile (**2a**) was obtained (66%) as a sole product. (iv) Oxygenation occurred stereoselectively, but the [3 + 2]cycloaddition did not.

---

† Electron-transfer from a TCNE radical anion to triplet oxygen is calculated to be endothermic by 26.7 kcal/mol (1 cal = 4.184 J). Generation of an oxygen radical anion by electron transfer is thus unfavoured. Cyclic voltammetric analyses of TCNE in the presence or absence of oxygen by Tokumaru and coworkers[7] support this assumption. Under the present irradiation conditions, singlet oxygen could be 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, cannot generate triplet oxirane nor TCNE since their triplet energies (estimated to be around 70 kcal/mol from their absorption spectra) are much higher than the energies stored in the radical ion pairs which are calculated to be 23.8, 28.4, 28.4, 28.6, and 36.4 kcal/mol, respectively, for (**1a**—**e**). Sensitisation by excited EDA complexes is also highly unlikely since such excited species are, generally very short-lived and rapidly converted into radical ion pairs.[8]

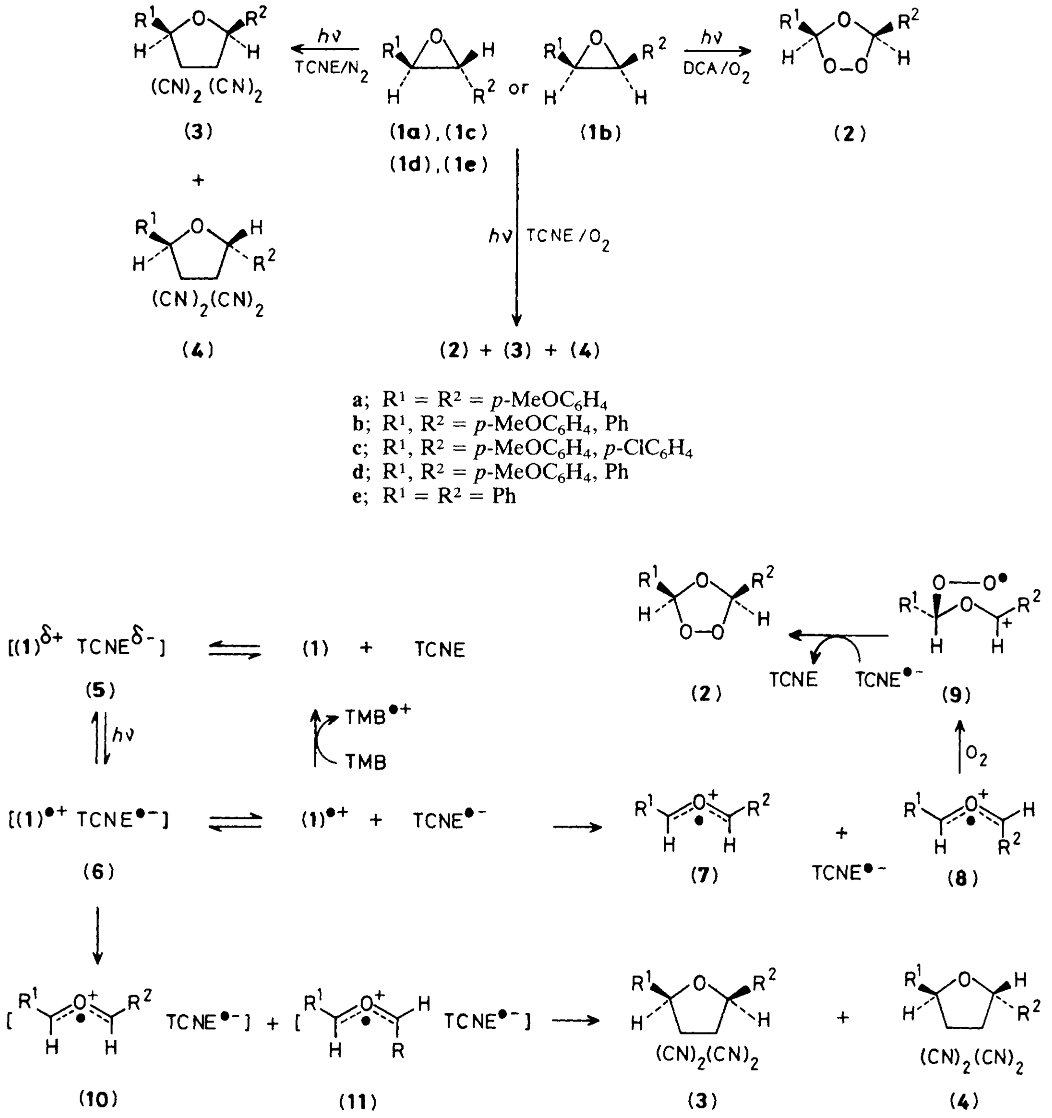
Indirect evidence which indicates the improbability of generating singlet oxygen under our oxygenation conditions is that TMB, used as a quencher and known to be labile to singlet oxygen,[9] remained unchanged and was recovered quantitatively; similar oxygenations occur even in the dark in the methylenecyclopropane–TCNE system.[1] The observed solvent polarity dependence and quenching by TMB would not be expected to occur by a singlet oxygen mechanism.[10]

Satisfactory elemental analyses and spectroscopic data were obtained for all compounds.

‡ ^{1}H N.m.r. (90 MHz, CDCl$_3$) δ: (**2b**) = (**2d**), 3.82 (3H, s), 6.25 (1H, s), 6.32 (1H, s), 6.80—7.07 (2H, m), 7.27—7.65 (7H, m); (**2c**), 3.82 (3H, s), 6.23 (1H, s), 6.31 (1H, s), 6.81—7.04 (2H, m), 7.28—7.61 (7H, m); (**3a**), 3.88 (6H, s), 5.52 (2H, s), 6.95—7.20 (4H, m), 7.43—7.70 (4H, m); (**4a**), 3.86 (6H, s), 5.91 (2H, s), 6.90—7.20 (4H, m), 7.38—7.65 (4H, m); (**3b**) = (**3d**), 3.87 (3H, s), 5.55 (2H, s), 6.98—7.17 (2H, m), 7.45—7.67 (7H, m); (**4b**) = (**4d**), 3.88 (3H, s), 5.94 (1H, s), 5.98 (1H, s), 6.97—7.20 (2H, m), 7.44—7.77 (7H, m); (**3c**), 3.86 (3H, s), 5.52 (1H, s), 5.55 (1H, s), 6.93—7.20 (2H, m), 7.45—7.70 (6H, m); (**4c**), 3.86 (3H, s), 5.92 (1H, s), 5.94 (1H, s), 6.90—7.20 (2H, m), 7.35—7.67 (6H, m); (**3e**), 5.65 (2H, s), 7.45 (10H, m); (**4e**), 6.03 (2H, s), 7.45—7.77 (10H, m).

§ Ohta and coworkers reported that (**1b**) and (**1e**) did not afford trioxolane,[3] but Schaap reported the formation of (**2e**) under DCA-biphenyl-cosensitized conditions.[4]

¶ The calculated Δ*G* values for the reactions of (**1**$^{\cdot+}$) with TMB are −8.5, −13.1, −13.1, −13.4, and −21.2 kcal/mol, respectively, for (**1a**—**e**) in dichloromethane. For instance, when (**1**) and TCNE (0.10 mmol each) are irradiated in the presence of TMB (0.10 mmol) in dichloromethane (3 ml), (**1a**) afforded (**3a**) and (**4a**) in 10 and 11% yields, respectively, and (**3b**) and (**4b**) were obtained in 10 and 8% yields, respectively, from (**1b**).



a; $R^1 = R^2 = p\text{-MeOC}_6H_4$
b; $R^1, R^2 = p\text{-MeOC}_6H_4$, Ph
c; $R^1, R^2 = p\text{-MeOC}_6H_4$, $p\text{-ClC}_6H_4$
d; $R^1, R^2 = p\text{-MeOC}_6H_4$, Ph
e; $R^1 = R^2 = $ Ph

Scheme 1

Table 1. Half-wave oxidation potentials, charge-transfer (C-T) absorptions, and yields of *cis*-trioxolanes (**2**) and the [3 + 2]cycloadducts (**3**) and (**4**).

				Yields and conversions in dichloromethane/%					
(**1**)[a]	$E^{ox}_{1/2}$/ V *vs.* s.c.e.[b]	C-T absorption/ nm in CH_2Cl_2		TCNE/ mmol	Reaction time/h	(**2**)	(**3**)	(**4**)	Conversion
(**1a**)	1.27	380	540	0.1	1	87			100
				0.02	3	80			100
(**1b**)	1.47	373	516	0.1	5	47	14	13	91
(**1c**)	1.47	364	518	0.1	2	94			100
				0.02	3	96			100
(**1d**)	1.48	366	520	0.1	1	99			100
				0.02	3	98			100
(**1e**)	1.82	374		0.1	10	8	6	15	79

[a] Concentration 0.1 mmol. [b] Measured by cyclic voltammetry at a platinum electrode in acetonitrile with 0.1 M tetraethylammonium perchlorate as a supporting electrolyte, s.c.e. = saturated calomel electrode.

The first three are features of photoexcitation reactions of EDA complexes of MCP with TCNE,[1] indicating the occurrence of two competitive pathways *via* the initially formed geminate radical ion pairs. The fact that the same stereoselectivity was observed for photo-oxygenation here as that observed under DCA-sensitised conditions is particularly interesting. Neither an oxygen radical anion nor singlet oxygen is generated in these cases, suggesting that singlet oxygen is not always responsible for the stereoselective oxygenation of oxiranes under DCA-sensitised conditions. This suggests that triplet oxygen as a direct source for oxygenation cannot be ruled out even under DCA-sensitised conditions. Gollnick recently concluded that triplet oxygen is responsible for the DCA-sensitised oxygenation of 1,1-di(*p*-methoxyphenyl)ethylene.[5]

A mechanism taking all these observations into account is proposed in Scheme 1. Diffusion of the photogenerated radical ion pair (**6**) to ($\mathbf{1}^{\cdot+}$) and TCNE$^{\cdot-}$ occurs much more efficiently for the more electron-donating (**1**) and in the more polar solvent.[1,2] From previously reported photoinduced electron-transfer reactions of oxiranes,[6] it is assumed that the ring cleavage of ($\mathbf{1}^{\cdot+}$) occurs nonstereoselectively to form (**7**) and (**8**), both of which, in turn, can be captured by triplet oxygen to form peroxy radical cations. In these the barrier to rotation around the C–O–C$^+$ bond is small, and so a second C–O bond formation can occur through the least hindered radical (**9**) to form ($\mathbf{2}^{\cdot+}$) exclusively. Back electron-transfer from the TCNE radical anion to ($\mathbf{2}^{\cdot+}$) forms (**2**) and TCNE. TCNE can then re-enter the EDA complex formation cycle. The nonstereoselective formation of (**3**) and (**4**) can be explained either by a concerted [3 + 2]cycloaddition of (**10**) and (**11**) or, more likely, by an alternative concerted addition of carbonyl ylides with TCNE after a back electron-transfer reaction has occurred within the cage. It was also confirmed that once the ring-opened radical cations (**7**) and (**8**) have diffused from the ion pair (**10**) and (**11**) the [3 + 2]cycloaddition cannot occur;[1] the cycloaddition can only occur *via* (**10**) and (**11**) within the solvent cage.[1,2]

Support from Kurata Foundation is gratefully acknowledged.

Received, 14th April 1986; Com. 485

References

1 T. Miyashi, M. Kamata, and T. Mukai, *J. Am. Chem. Soc.*, 1986, **108**, 2755.

2 J. M. Masnovi, A. Levine, and J. K. Kochi, *J. Am. Chem. Soc.*, 1985, **107**, 4356.

3 S. Futamura, S. Kusunose, H. Ohta, and Y. Kamiya, *J. Chem. Soc., Chem. Commun.*, 1982, 1223; S. Futamura, S. Kusunose, H. Ohta, and Y. Kamiya, *J. Chem. Soc., Perkin Trans. 1*, 1984, 15.

4 A. P. Schaap, S. Siddiqui, S. D. Gagnon, and L. Lopez, *J. Am. Chem. Soc.*, 1983, **105**, 5149; A. P. Schaap, S. Siddiqui, G. Prasad, A. F. M. M. Rahman, and J. P. Oliver, *J. Am. Chem. Soc.*, 1984, **106**, 6087.

5 K. Gollnick and A. Schnatterer, *Tetrahedron Lett.*, 1984, 185.

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

7 R. Akaba, H. Sakuragi, and K. Tokumaru, *Tetrahedron Lett.*, 1984, 1677.

8 E. H. Hilinski, J. M. Masnovi, C. Amatore, J. K. Kochi, and P. M. Rentzepis, *J. Am. Chem. Soc.*, 1983, **105**, 6167; E. H. Hilinski, J. M. Masnovi, J. K. Kochi, and P. M. Rentzepis, *ibid.*, 1984, **106**, 1984.

9 I. Saito and T. Matsuura, *Tetrahedron Lett.*, 1970, 4987; I. Saito, M. Imuta, and T. Matsuura, *Tetrahedron*, 1972, **28**, 5313.

10 J. Eriksen and C. S. Foote, *J. Am. Chem. Soc.*, 1980, **102**, 6083.