Electron-Transfer-Induced Photorearrangements and Photooxygenations of 1,1,2,3-Tetraarylcyclopropanes

Klaus Gollnick* and Uwe Paulmann

Institut für Organische Chemie der Universität München, Karlstr. 23, D-8000 München 2, West Germany

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1,1-Diaryl-*trans*-2,3-diphenylcyclopropanes **3a–e** and *trans*-2,3-diaryl-1,1-diphenylcyclopropanes **3f–i** were prepared by di-π-methane rearrangement of 1,1-diaryl-3,3-diphenylpropenes **2a–e** and 3,3-diaryl-1,1-diphenylpropenes **2f–i**, respectively. In nonpolar and in polar solvents, tetraarylcyclopropanes **3a–i** are inert toward singlet oxygen. In the presence of 9,10-dicyanoanthracene (DCA), irradiation of cyclopropanes **3a–e** in O_2-saturated acetonitrile (MeCN) solutions yield oxygenation products: benzophenone and benzaldehyde as main products from **3a**, 1,2-dioxolanes **4b–e** from **3b–e**. Cyclopropanes **3f–i**, however, rearrange to 3,3-diaryl-1,1-diphenylpropenes **2f–i** under these conditions. When irradiated in the presence of DCA or 1,8-dihydroxyanthraquinone (1,8-AQ) in deoxygenated MeCN solutions, cyclopropanes **3a–e** remain unchanged, whereas cyclopropanes **3f–i** rearrange to propenes **2f–i**. By using biphenyl and lithium perchlorate as additives in DCA-sensitized reactions, photooxygenations of **3a–e** as well as photorearrangements of **3f–i** are shown to proceed as electron-transfer-induced reactions via 1,3-radical cations formed by ring opening, occurring in all cases exclusively between carbon atoms C-1 and C-2 of these cyclopropanes. Small amounts of benzoquinone quench the DCA-sensitized oxygenation of cyclopropanes **3a–e** completely, and 1,8-AQ is incapable of sensitizing the oxygenation of these cyclopropanes, indicating that electron-transfer-induced oxygenations of 1,1,2,3-tetraarylcyclopropanes need superoxide radical anion, $O_2^{\bullet-}$, as the oxygenating species. A mechanism is proposed according to which the cationic sites of the 1,3-radical cation intermediates determine whether the respective radical cation rearranges rapidly by 1,2-aryl migration to the corresponding 1,1,3,3-tetraarylpropene or is long lived enough to undergo a bimolecular reaction with $O_2^{\bullet-}$ to yield the corresponding 1,2-dioxolane.

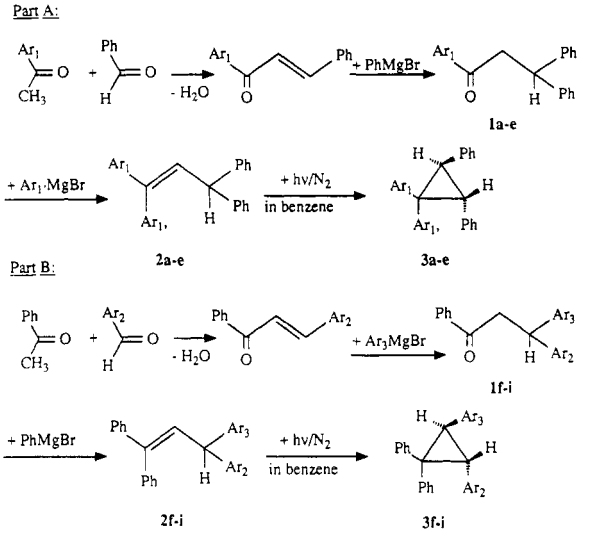
Introduction

In the preceding paper,[1] we studied the electron-transfer-induced photooxygenation of 1,1,2,2-tetraarylcyclopropanes[2] and of 1,1,3,3-tetraarylpropenes. Oxygenation rates and oxygenation products as well as rearrangements of the cyclopropanes turned out to depend strongly on the nature and number of the electron-donating aryl groups. These results prompted us to explore the electron-transfer-induced photoreactions of 1,1,2,3-tetraarylcyclopropanes in deoxygenated as well as in oxygen-saturated acetonitrile solutions. As with 1,1,2,2-tetraarylcyclopropanes, we find a rather strong dependence of oxygenation rates, oxygenation products, and rearrangements of 1,1,2,3-tetraarylcyclopropanes on the nature, number, and position of the electron-donating aryl groups.

Results

Synthesis of 1,1,2,3-Tetraarylcyclopropanes. 1,1-Diaryl-2,3-diphenylcyclopropanes **3a–e** and 2,3-diaryl-1,1-diphenylcyclopropanes **3f–i** were prepared as outlined in Scheme I, parts A and B, respectively. According to known procedures, condensation of acetophenones (A, $Ar_1C(O)CH_3$; B, $PhC(O)CH_3$) with aromatic aldehydes (A, PhCHO; B, Ar_2CHO) led to chalcones, $Ar_1C(O)CH{=}CHPh$ and $PhC(O)CH{=}CHAr_2$, which were treated with Grignard reagents (A, PhMgBr; B, Ar_3MgBr) to afford 1-aryl-3,3-diphenyl-1-propanones **1a–e** (part A) and 3,3-diaryl-1-phenyl-1-propanones **1f–i** (part B). Ketones **1** reacted with Grignard reagents (A, Ar_1MgBr; B, PhMgBr) to yield 1,1-diaryl-3,3-diphenylpropenes **2a–e** (part A) and 3,3-diaryl-1,1-diphenylpropenes **2f–i** (part B). Propenes **2**, irradiated in nitrogen-saturated benzene solution with UV light, underwent di-π-methane rearrangements[3] to 1,1-diaryl-2,3-diphenylcyclopropanes **3a–e** (part A) and 2,3-diaryl-1,1-diphenylcyclopropanes **3f–i** (part B), isolated in satisfying yields. We interrupted the photochemical reactions after about 70 to 80% of propene **2** had rearranged to cyclopropane **3**, because if we continued the irradiation, the production of polymeric material made the isolation of **3** more difficult.

Scheme I. Synthesis of 1,1,*trans*-2,3-Tetraarylcyclopropanes: Part A, 1,1-Diaryl-*trans*-2,3-diphenylcyclopropanes; Part B, *trans*-2,3-Diaryl-1,1-diphenylcyclopropanes



In 1965, Griffin[4] reported that UV irradiation of 1,1,3,3-tetraphenylpropene (**2a**) in benzene gave rise to 1,1,*trans*-2,3-tetraphenylcyclopropane (**3a**).

Cyclopropanes **3a** through **3i** of Scheme I exhibited one set of the respective ^{13}C NMR signals for each cyclopropane, showing that only one of the two possible configurational isomers was formed at each time. An X-ray analysis of cyclopropane **3e** revealed its trans configuration. We assume therefore that all the cyclopropanes **3a–i** represent the trans isomers.

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(2) For earlier studies on 1,1,2,2-tetraarylcyclopropanes, see: (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) Miyashi, T.; Kamata, M.; Mukai, T. *J. Am. Chem. Soc.* **1987**, *109*, 2780.

(3) (a) Döpp, D.; Zimmerman, H. E. In *Houben-Weyl, Methoden der Organischen Chemie, Photochemie I*, Vol. 4, Part 5a; Müller, E., Ed.; Georg Thieme Verlag: Stuttgart, 1975; p 413. (b) Zimmerman, H. E.: Hixon, S. S.; Mariano, P. S. *Chem. Rev.* **1973**, *73*, 531. (c) Hixon, S. S. *Tetrahedron Lett.* **1972**, 1155.

(4) Griffin, E. W.; Marcantonio, A. F.; Kristensson, H. *Tetrahedron Lett.* **1965**, 2951.

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Table I. Oxidation Potentials of 1,1,3,3-Tetraarylpropenes 2 and 1,1,*trans*-2,3-Tetraarylcyclopropanes 3 and DCA Fluorescence Quenching Constants k_q of 1,1,*trans*-2,3-Tetraarylcyclopropanes 3 in Acetonitrile

	R[a] in						k_q of 3 (10^{10}/M s)	
compd	Ar_1	$Ar_{1'}$	Ar_2	Ar_3	E_{ox} of 2 (V)[b]	E_{ox} of 3 (V)[b]	exp	calcd
a	H	H			1.71	1.54	1.03	1.29
b	Me	H			1.65	1.48[c]	*d*	1.32
c	Me	Me			1.62	1.43	1.15	1.36
d	OMe	H			1.42	1.37	1.30	1.37
e	OMe	OMe			1.38	1.28	1.40	1.40
f			Me	H	1.72	1.47[c]	*d*	1.32
g			Me	Me	1.67	1.42	1.23	1.36
h			OMe	H	1.65	1.31	1.33	1.39
i			OMe	OMe	1.63	1.16	1.63	1.43

[a] Ar = 4-R-C_6H_4. [b] Irreversible oxidation potentials in MeCN (vs SCE); scan rate 400 mV/s; standard 1,3,5-trimethoxybenzene, $E_{ox}^{1/2}$ = 1.49 V.[6] [c] Compound contains traces of impurities. [d] Not determined.

Table II. DCA-Photosensitized Oxygenation of 1,1-Diaryl-*trans*-2,3-diphenylcyclopropanes 3a–e in Oxygen-Saturated Acetonitrile[a]

	R[b] in				r_0[e] (mL/	
3	Ar_1	$Ar_{1'}$	$[3]_0$[c] (M)	additive[d] (M)	min)	t[f] (h)
a	H	H	0.025		*g*	6
				Bp 0.025	*g*	1.7
				Bp 0.025 +Bq 0.003	*h*	*h*
b	Me	H	0.025	Bp 0.025	0.10	2.0
				Bq 0.003	*h*	*h*
				i	*h*	*h*
c	Me	Me	0.013		*g*	26
				Bp 0.025	0.05	2.0
				Lp 0.025	0.03	4.0
				Bq 0.003	*h*	*h*
				i	*h*	*h*
d	OMe	H	0.025		0.05	4.0
				Bp 0.025	0.15	1.3
				Lp 0.025	0.09	2.3
				Bq 0.003	*h*	*h*
				i	*h*	*h*
e	OMe	OMe	0.025		0.15	1.3
				Bp 0.025	0.40	0.5
				Lp 0.025	0.20	1.0
				Bq 0.003	*h*	*h*
				i	*h*	*h*

[a] Irradiations carried out at room temperature in the 25-mL irradiation unit (see Experimental Section). [b] Ar = 4-R-C_6H_4. [c] Initial concentration of 3. [d] Bp = biphenyl; Lp = $LiClO_4$; Bq = *p*-benzoquinone. [e] Initial rate of oxygen consumption. [f] Time required for the consumption of 1 molar equiv of O_2. [g] S-shaped O_2-uptake curve. [h] No oxygen consumption during several hours of irradiation. [i] Sensitizer: 1,8-AQ, 3×10^{-4} M.

Table III. DCA-Photosensitized Rearrangement of *trans*-2,3-Diaryl-1,1-diphenylcyclopropanes 3f–i into 3,3-Diaryl-1,1-diphenylpropenes 2f–i in Acetonitrile[a]

	R[b] in				irradiation under N_2		irradiation under O_2	
3	Ar_2	Ar_3	$[3]_0$[c] (M)	add.[d]	t (h)	2 (%)	t (h)	2 (%)
f[e]	Me	H	0.025	Bp	4	25	1	20
g	Me	Me	0.013		13	60	1	45
				Bp	8	38	1	100
				f	19	32	1	28
h	OMe	H	0.025		19	26	1	91
				Bp	19	45	1	100
				2a	19	55	1	100
				Bq	19	44	1	100
				f	19	10	3	100
i	OMe	OMe	0.025		13	100	1	100
					0.5	23	0.5	100
				Bp	0.5	46	0.5	100
				2a	0.5	76	0.5	100
				Bq	0.5	46	0.5	90
				f	0.5	29	0.5	24

[a] Irradiations carried out at 13 °C in the 25-mL irradiation unit as described in the Experimental Section. [b] Ar = 4-R-C_6H_4. [c] Initial concentration of 3. [d] Additive: Bp = biphenyl, 0.025 M; Bq = *p*-benzoquinone, 0.025 M; [**2a**] = 0.025 M. [e] Compound contains traces of impurities. [f] Sensitizer: 1,8-AQ, 3×10^{-4} M.

Oxidation Potentials of and DCA Fluorescence Quenching by 1,1,2,3-Tetraarylcyclopropanes. Oxidation potentials of tetraarylpropenes **2a–i** and tetraarylcyclopropanes **3a–i** were determined in acetonitrile (MeCN) solutions by cyclic voltammetry (Table I).

Quenching of the DCA fluorescence by the cyclopropanes **3a–i** was executed for nitrogen-saturated MeCN solutions. DCA was excited at 383 nm. The intensities of the DCA fluorescence emission at 450 nm were determined for at least six different concentrations of the respective cyclopropane (between about 0.002 and 0.03 M). Fluorescence quenching constants k_q were obtained from the slopes of Stern–Volmer plots, $k_q\tau_{DCA}$, with τ_{DCA} = 15.3 ns in MeCN[5] by applying the method of the least squares (Table I).

The oxidation potentials, E_{ox}, of propenes **2a–i** as well as of cyclopropanes **3a–i** are irreversible. E_{ox}(**3**) of the cyclopropane is always lower than E_{ox}(**2**) of the corresponding propene. By using the irreversible oxidation potentials,[7] the free enthalpy changes, ΔG, were calculated by applying eq 1[9]

$$\Delta G = 23.06[E_{ox}(3) - E_{red}^{1/2}(DCA) - e_0^2/\epsilon r - E_{0,0}(DCA)] \text{ (kcal/mol)} \quad (1)$$

with $E_{red}^{1/2}$(DCA) = −0.89 V, $E_{0,0}$(DCA) = 2.88 eV, and $e_0^2/\epsilon r$ = 0.06 eV in MeCN.[10]

The experimental k_q values of DCA fluorescence quenching by **3** agree well with those calculated (Table I) by using eq 2

$$k_q = (2 \times 10^{10})[1 + 0.25[\exp(\Delta G^{\ddagger}/RT) + \exp(\Delta G/RT)]]^{-1} \ (M^{-1}\ s^{-1}) \quad (2)$$

(5) Manring, L. E.; Gu, C. I.; Foote, C. S. *J. Phys. Chem.* **1983**, *87*, 40.
(6) Zweig, A.; Hodgson, W. G.; Jura, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 4124.

(7) Since the oxidation potentials are irreversible, the ΔG values obtained should be only approximate. However, they appear to agree generally quite well with experiment.[8]
(8) (a) Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 6083. (b) Araki, Y.; Dobrowolsky, D. C.; Goyne, T. E.; Hanson, D. C.; Jiang, Z. Q.; Lee, K. J.; Foote, C. S. *J. Am. Chem. Soc.* **1984**, *106*, 4570. (c) Gollnick, K.; Schnatterer, A. *Photochem. Photobiol.* **1986**, *43*, 365.
(9) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
(10) Mattes, S. L.; Farid, S. In *Organic Photochemistry*, Vol. 6; Padwa, A., Ed.; Marcel Dekker: New York, 1983; p 233.

with $\Delta G^{\ddagger} = [[\Delta G/2]^2 + [\Delta G^{\ddagger}(0)]^2]^{1/2} + \Delta G/2$ and $\Delta G^{\ddagger}(0) = 2.4$ kcal/mol.[9]

1,8-Dihydroxyanthraquinone (1,8-AQ) was also used as a sensitizer (Tables II and III). With $E_{red}^{1/2} = -0.64$ V and $E_{0,0} = 2.49$ eV for its singlet excited state in MeCN,[11] $\Delta G \leq 0$ is calculated for substrates whose oxidation potential E_{ox} is less than 1.9 V. Electron transfer between singlet excited 1,8-AQ and cyclopropanes **3a–i** should therefore occur with rates about as fast as those with ^{1}DCA*.[12]

Irradiation of 1,1,2,3-Tetraarylcyclopropanes in the Presence of O_2 and Various Sensitizers. Effects of Additives. In order to survey the behavior of tetraarylcyclopropanes **3a–i** under various oxygenation conditions, we irradiated these substrates in a 25-mL irradiation unit with automatic registration of oxygen consumption in O_2-saturated solutions of CCl_4 and MeCN by using for sensitization tetraphenylporphin (TPP) in CCl_4, rose bengal (RB) and 1,8-AQ in MeCN, and DCA in CCl_4 as well as in MeCN. The effects of additives such as biphenyl (Bp), lithium perchlorate (Lp), and *p*-benzoquinone (Bq) were studied for DCA-sensitized reactions in MeCN.

In *CCl_4*, none of the cyclopropanes absorbed oxygen during irradiation for several hours in the presence of TPP or DCA. ^{1}H and ^{13}C NMR analyses of the solutions showed that the cyclopropanes remained unchanged under these conditions. TPP as well as DCA are efficient sensitizers for the production of singlet oxygen in CCl_4.[8c] Thus, as expected, 1,1,2,3-tetraaryl-substituted cyclopropanes proved to be as incapable of reacting with singlet oxygen as 1,1,2,2-tetraarylcyclopropanes.[1]

In *MeCN*, a very slow oxygen consumption was observed with cyclopropane **3e** in the presence of RB, whereas no oxygen uptake occurred with the other cyclopropanes during several hours of irradiation, and the cyclopropanes remained unchanged (NMR spectra). Again, this result agrees well with the inertness of the cyclopropanes toward singlet oxygen.

However, if DCA was used as a sensitizer, cyclopropanes **3a–e** absorbed O_2 with appreciable rates at the beginning of the reaction (Table II). These rates continuously decreased during the consumption of the respective cyclopropane and approached a value of nearly zero after about 1 molar equiv of O_2 was consumed. ^{1}H and ^{13}C NMR spectra confirm the formation of oxygenated products at the expense of the starting cyclopropanes.

Due to the co-sensitizing effect of Bp[14] and the special salt effect of Lp,[15] both these additives are expected to enhance the rates of electron-transfer processes. Benzoquinone ($E_{red}^{1/2} = -0.51$ V[16]), however, should efficiently abstract an electron not only from superoxide radical anion, $O_2^{\bullet-}$,[17] but also from DCA$^{\bullet-}$, since $\Delta G = E_{red}(Bq) - E_{red}(DCA) = -0.38$ V. Therefore, Bq should quench those electron-transfer-induced oxygenations that proceed via reactions of radical cations with $O_2^{\bullet-}$.[18]

As Table II shows, initial oxygenation rates, r_0, increase and the irradiation periods needed for absorption of 1 molar equiv of oxygen decrease in the presence of Bp and $LiClO_4$, when these additives are applied at concentrations comparable to that of O_2 (= 8.1×10^{-3} M for O_2-saturated MeCN[19]) and to those of **3** at the beginning of the reactions. On the other hand, relatively small concentrations of Bq are sufficient to quench the oxygenation reactions completely (Table II).

1,8-AQ is not only a sensitizer of singlet oxygen reactions[20,21] but also of electron-transfer-induced oxygenations that occur as chain reactions, which involve interactions between radical cations and $^3O_2$ (see, for example, the preceding paper on electron-transfer-induced oxygenations of 1,1,2,2-tetraarylcyclopropanes[1]). Electron-transfer oxygenations, however, that proceed via superoxide radical anions, $O_2^{\bullet-}$, are not sensitized by 1,8-AQ.[22] *trans*-2,3-Diaryl-1,1-diphenylcyclopropanes **3a–e** remained unchanged (according to ^{1}H NMR analyses) and no oxygen consumption occurred during irradiation of their O_2-saturated MeCN solutions in the presence of 1,8-AQ for several hours (Table II).

In contrast to cyclopropanes **3a–e**, MeCN solutions of cyclopropanes **3f–i** did not consume any oxygen during several hours of irradiation in the presence of DCA.

Moreover, in contrast to the results obtained with RB as a sensitizer in MeCN, the cyclopropanes **3f–i** did not remain unchanged in the presence of DCA. According to the ^{1}H and ^{13}C NMR spectra of the solutions, **3f–i** were rearranged to the corresponding 1,1,3,3-tetraarylpropenes **2f–i**.

Similar observations were made with 1,8-AQ as a sensitizer: no oxygen uptake occurred during several hours of irradiation, but cyclopropanes **3f–i** were rearranged to the corresponding 3,3-diaryl-1,1-diphenylpropenes **2f–i** as in the presence of DCA.

Although propenes **2f–i** are slowly oxygenated in the presence of DCA in O_2-saturated MeCN solutions,[1] they remained unchanged in the presence of **3f–i** as long as these cyclopropanes were not rearranged to ≥95%. Obviously, **3f–i** exert a protective function on the electron-transfer-induced photooxygenation of **2f–i**. In turn, **2f–i** should exert a rate-enhancing effect on the electron-transfer-induced rearrangement of **3f–i**. However, not only propenes **2f–i** but also propenes **2a–e** should be able to enhance the DCA-photosensitized rearrangements of cyclopropanes **3f–i** by acting in the same manner as biphenyl (Bp), i.e., as a co-sensitizer. By using propene **2a** as a "co-sensitizer"[23] at the same concentration as Bp, **2a** ap-

(11) Kawenoki, I.; Keita, B.; Kossanyi, J.; Nadjo, L. *Nouv. J. Chim.* **1982**, *6*, 387.

(12) However, the singlet lifetime of ^{1}(1,8-AQ)* in MeCN, reported to be $\tau_s = 0.7$ ns,[13] is about 20 times shorter than that of ^{1}DCA* ($\tau_s = 15.3$ ns). This result should make ^{1}(1,8-AQ)* a much less efficient sensitizer than DCA for electron-transfer reactions: for a diffusion-controlled quenching of a singlet excited state by a quencher Q, the half-value concentration of the quencher is given by $[Q]_{1/2} = k_q\tau_s$. Thus, for quenching of ^{1}(1,8-AQ)*, $[Q]_{1/2}$ should be about 20 times larger for ^{1}(1,8-AQ)* quenching than for ^{1}DCA* quenching.

To our knowledge, the triplet energy of 1,8-AQ is not yet known. However, the triplet quinone is probably capable for a successful electron-transfer process (Gollnick; et al., unpublished).

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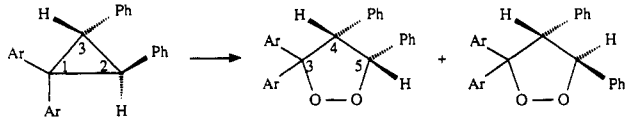
(22) Gollnick, K.; Schnatterer, A.; Utschick, G.; Paulmann, U.; Held, S. In *Light in Biology and Medicine*, Vol. 1; Douglas, R. H., Moan, J., Dall'Acqua, F., Eds.; Plenum Press: New York, 1988; p 67.

(23) The term "co-sensitizer", introduced by Schaap,[2b] seems to be well-accepted. We have used, therefore, this term in this paper as well as in the preceding paper[1] for the action of Bp in DCA-photosensitized oxygenation reactions. However, we prefer the term "electron-transfer mediator",[8c] because in a secondary electron-transfer reaction such as $A^{\bullet+} + B \rightarrow A + B^{\bullet+}$, with $E_{ox}(A) > E_{ox}(B)$, B "quenches" the reactions of $A^{\bullet+}$, whereas $A^{\bullet+}$ "mediates" the reactions of $B^{\bullet+}$.

Scheme II. 1,2-Dioxolanes from 1,1-Diaryl-*trans*-2,3-diphenylcyclopropanes



3	cis-4	trans-4
c: Ar = 4-Me-C_6H_4	70 %	30 %
e: Ar = 4-MeO-C_6H_4	60 %	40 %

parently increases the photorearrangement rates to an even larger extent as does Bp (Table III).

Irradiation of 1,1,2,3-Tetraarylcyclopropanes in the Presence of DCA and 1,8-AQ in Deoxygenated MeCN Solutions. The results obtained with oxygen-saturated MeCN solutions prompted us to explore the irradiation of cyclopropanes **3a–i** with DCA and 1,8-AQ in deoxygenated MeCN solutions.

Under these conditions, cyclopropanes **3a–e** remained completely unaltered, even after 30 h of irradiation. Addition of Bp, $LiClO_4$, or Bq had no effect on these results.

Cyclopropanes **3f–i**, on the other hand, gave rise to the same tetraarylpropenes **2f–i**, respectively, as were found in O_2-saturated solutions, though with noticeably *slower rates under nitrogen than under oxygen* in DCA- as well as in 1,8-AQ-photosensitized reactions. Addition of Bp, Bq, and **2a** enhanced the rates of DCA-photosensitized rearrangements of these cyclopropanes (Table III).

Photooxygenation Products. 3,3-Diaryl-4,5-diphenyl-1,2-dioxolanes. In order to obtain appreciable amounts of products, we irradiated cyclopropanes **3a–e** in a 200-mL irradiation unit with DCA as a sensitizer in O_2-saturated solutions of MeCN. A filter solution was used, which cut-off all wavelengths shorter than 405 nm (Experimental Section). Progress of the reaction was followed by ^1H NMR analyses of samples drawn during the irradiation period.

3,3-Bis(4-methoxyphenyl)-4,5-diphenyl-1,2-dioxolanes (*cis*-4e and *trans*-4e). When 1,1-bis(4-methoxyphenyl)-*trans*-2,3-diphenylcyclopropane (**3e**) had disappeared, irradiation was stopped. Removal of MeCN led to an oil whose ^1H NMR spectrum indicated the presence of four OCH_3 groups, two of which should belong to 1,2-dioxolane *cis*-**4e**, the other two should be due to 1,2-dioxolane *trans*-**4e**.

From ethanol, one of the isomers was obtained as a single crystalline product, mp 110–111 °C. It exhibited two OCH_3 groups with ^1H NMR singlets at δ 3.57 and 3.75, and two doublets, each representing one H atom, at δ 4.69 and 5.59 with coupling constants of 5.5 Hz.

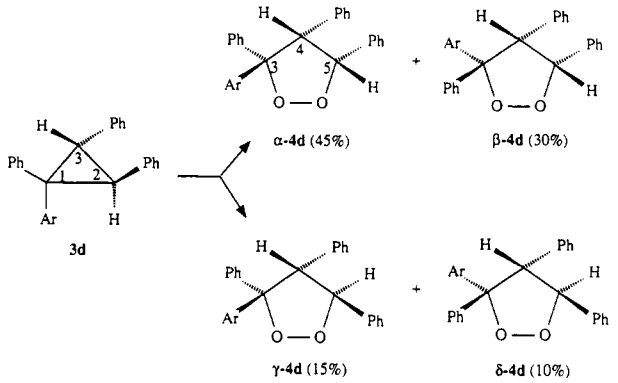
The other isomer could not be obtained as a crystalline compound. Its ^1H NMR spectrum showed two OCH_3 singlets at δ 3.65 and 3.73, and two doublets (1 H each) at δ 4.68 and 5.48 with coupling constants of 9 Hz.

Because of the smaller coupling constants, we attribute the cis configuration to the isomer of mp 110–111 °C (see Scheme II).

Since the ring protons appear exclusively as doublets, ring opening during the electron-transfer photooxygenation obviously occurs only between C-1 and C-2 (or the equivalent carbon atom C-3) of cyclopropane **3e**. If ring opening would occur between C-2 and C-3, the 1,2-dioxolane derived from this intermediate should have two identical ring protons expected to appear as a singlet at about δ 5.5 to 5.6.

The original product mixture, obtained after MeCN removal and resolution of the residue in $CDCl_3$, showed a 3:2 ratio of *cis*-**4e**:*trans*-**4e** according to peak heights

Scheme III. 1,2-Dioxolanes from *trans*-1-(4-Methoxyphenyl)-1,2,3-triphenylcyclopropane



(rather than to the integrals) of the corresponding OCH_3 singlets in the ^1H NMR spectrum.

3,3-Bis(4-methylphenyl)-4,5-diphenyl-1,2-dioxolanes (*cis*-4c and *trans*-4c). **3e** had disappeared from the solution after about 1 h of irradiation. Under the same reaction conditions, 1,1-bis(4-methylphenyl)-*trans*-2,3-diphenylcyclopropane (**3c**) needed 20 h for complete oxygenation. Removal of MeCN yielded an oil, which showed two pairs of CH_3 singlets, one at δ 2.10 and 2.31, the other at δ 2.13 and 2.34 in a (peak height) ratio of about 7:3 in its ^1H NMR spectrum. This observation shows that **3c** displays a similar behavior as **3e** in the photooxygenation reaction.

From *n*-hexane, a single crystalline product was obtained, mp 123–124 °C, whose ^1H NMR spectrum contained, in addition to the two CH_3 singlets at δ 2.10 and 2.31, two doublets (1 H each) at δ 4.75 and 5.59 with a coupling constant of 6 Hz.

The other isomer showed two CH_3 singlets at δ 2.13 and 2.34 and two doublets (1 H each) at δ 4.71 and 5.48 with a coupling constant of 10 Hz.

Again, because the ring protons exhibited different chemical shifts and appeared as doublets, ring opening of **3c** occurred exclusively between C-1 and C-2 (or C-3). Furthermore, because of the smaller coupling constant, the cis configuration is attributed to the crystalline isomer of mp 123–124 °C. The product ratio of *cis*-**4c**:*trans*-**4c** is therefore 7:3, i.e., similar to that obtained for dioxolanes **4e** (see Scheme II).

The same results were obtained when **3c** was photooxygenated in the presence of 1 molar equiv of biphenyl. However, in this instance, the irradiation time for complete oxygenation was reduced to 3 h.

3-(4-Methoxyphenyl)-3,4,5-triphenyl-1,2-dioxolanes (4d). If ring opening occurs between C-1 and C-2 (or C-3) but not between C-2 and C-3, two pairs of stereoisomeric 1,2-dioxolanes **4d** may be expected from 1-(4-methoxyphenyl)-1,2,3-triphenylcyclopropane (**3d**) (Scheme III): one pair having the two phenyl groups at C-4 and C-5 always cis oriented to each other, the other pair bearing these phenyl groups always trans disposed to each other. Furthermore, in each pair, one isomer contains the phenyl group at C-3 in a cis arrangement with respect to the phenyl group at C-4, whereas the other isomer exhibits a trans disposition of these two phenyl groups.

And indeed, four OCH_3 groups are displayed in the ^1H NMR spectrum of the residue obtained after **3d** had reacted with oxygen in a DCA-photosensitized oxygenation reaction. The OCH_3 singlets appeared at δ 3.77, 3.57, 3.82, and 3.65 in a (peak height) ratio of 9:6:3:2, which are attributed to 1,2-dioxolanes α-**4d**, β-**4d**, γ-**4d**, and δ-**4d**, respectively (Scheme III).

The assignments are based on the following observations: after about 5 h of irradiation of **3d** under similar conditions as were applied to **3e**, cyclopropane **3d** was quantitatively oxygenated to 1,2-dioxolanes. The residue, obtained after MeCN removal and attempted crystallization from ethanol, gave rise to a gel in a yield of about 64%, which, according to its ^1H NMR spectrum, contained two isomeric dioxolanes in a ratio of 3:2 as determined from the ratio of the OCH_3 singlet peak heights at δ 3.77 and 3.57. Furthermore, the spectrum showed two pairs of doublets (for 4 tertiary hydrogens altogether) in a 3:2 ratio, the first pair appearing at δ 4.73 and 5.62 with a coupling constant of 6 Hz and the second pair appearing at δ 4.73 and 5.56, also with a coupling constant of 6 Hz. Because both isomers show coupling constants of 6 Hz, we assume that the hydrogens (and consequently the phenyl groups) at C-4 and C-5 of both these isomers are cis-arranged with respect to each other (α-**4d** and β-**4d** of Scheme III).

Our further assignment, [(3*S*,4*S*,5*S*)/(3*R*,4*R*,5*R*)] (= α-**4d**) to the major and [(3*R*,4*S*,5*S*)/(3*S*,4*R*,5*R*)] (= β-**4d**) to the minor compound, rests on the following argument: in *cis*-1,2-bis(4-methoxyphenyl)cyclopropane, the OCH_3 singlet is located at δ 3.60; in the trans isomer, the OCH_3 singlet is shifted to 3.70.[15] In **3e**, where each anisyl group has a *cis*- as well as a *trans*-phenyl group as a next neighbor, the OCH_3 singlet appears at an "averaged value" of δ 3.65. In dioxolane *cis*-**4e**, one of the anisyl groups at C-3 has a *cis*-phenyl group as a next neighbor, whereas for the other anisyl group at C-3 the phenyl group at C-4 is trans-arranged. The OCH_3 groups of *cis*-**4e** exhibit singlets at δ 3.57 and 3.75, and therefore, according to the examples discussed, the anisyl group cis to the phenyl group at C-4 should show the "high field" singlet at 3.57, and, consequently, the anisyl group with trans disposition with respect to the C-4-phenyl group should occur as the "low field" singlet at 3.75. Thus, α-**4d**, having the anisyl group at C-3 in trans disposition to the C-4-phenyl group, should exhibit the OCH_3 singlet as the lower field value, i.e., at δ 3.77, whereas the β-**4d** isomer, with the anisyl group cis to the C-4-phenyl group, should exhibit the higher field singlet, i.e., at 3.57.

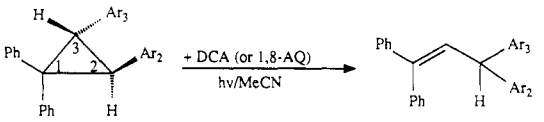
Unfortunately, the other two stereoisomers, γ-**4d** and δ-**4d**, could not be obtained free from the α- and β-**4d** isomers. The existence of the γ- and δ-isomers in the product mixture was shown, however, by the occurrence of the OCH_3 singlets at δ 3.65 and 3.82 in a 3:2 ratio. With regard to our discussion above, we assume a [(3*S*,4*S*,5*R*)/(3*R*,4*R*,5*S*)] configuration (= γ-**4d**) for the isomer with the OCH_3 singlet at δ 3.82 and a [(3*R*,4*S*,5*R*)/(3*S*,4*R*,5*S*)] configuration (= δ-**4d**) for that with the OCH_3 singlet at 3.65.

The two pairs of dioxolanes, (α-**4d** + β-**4d**) and (γ-**4d** + δ-**4d**), are formed in a 3:1 ratio. Thus, dioxolane formation from **3d** resembles those from **3c** and **3e** in that, in all these cases, dioxolanes with cis-arranged phenyl groups at C-4 and C-5 represent the major products (60–75%), whereas dioxolanes with trans-disposed phenyl groups represent the minor products (40–25%).

As with **3c**, the irradiation period for complete oxygenation of **3d** could be reduced, from about 5 h to about 1 h, if 1 molar equiv of biphenyl was added to the reaction mixture. Products and product ratios, however, remained unchanged by this addition.

3-(4-Methylphenyl)-3,4,5-triphenyl-1,2-dioxolanes (4b). Photooxygenation of 1-(4-methylphenyl)-1,*trans*-2,3-triphenylcyclopropane (**3b**) was carried out in the presence of 1 molar equiv of Bp as co-sensitizer. After about 95% of 1 mol of O_2 per mol of **3b** was absorbed, the solution was worked up. The ^1H NMR spectrum of the residue revealed the presence of benzaldehyde and 4-methylbenzophenone (methyl protons at δ 2.35) as well as of some 1,2-dioxolanes (methyl protons between δ 2.1 and 2.4). One of these dioxolanes could be isolated by chromatography, followed by recrystallization from ethanol. Its methyl protons appear at δ 2.13 and its tertiary protons at 4.75 and 5.56 with coupling constants of J = 6 Hz, indicating that this dioxolane is either the α-**4b** or the β-**4b** compound, i.e., one of the "*cis*"-dioxolanes (compare the corresponding dioxolanes **4d** of Scheme III). Whereas the ratio of the carbonyl compounds to the dioxolanes is about 3:2 (assuming that the methyl proton signals appearing in the range of δ 2.1 to 2.4 belong to the dioxolanes except that a 2.35), the ratio of the (four expected) dioxolanes α- through δ-**4b** could not be determined. This is so, because, on the one hand, we were not able to isolate the other dioxolanes and, on the other hand, apart from benzaldehyde, 4-methylbenzophenone, and dioxolanes, there are obviously some other, unidentified oxidation products present, though in minor amounts.

Scheme IV. Electron-Transfer-Induced Photorearrangement of *trans*-2,3-Diaryl-1,1-diphenylcyclopropanes



3 2

f: Ar_2 = 4-Me-C_6H_4; Ar_3 = Ph;
g: Ar_2 = Ar_3 = 4-Me-C_6H_4;
h: Ar_2 = 4-MeO-C_6H_4; Ar_3 = Ph;
i: Ar_2 = Ar_3 = 4-MeO-C_6H_4.

Photooxygenation of 1,1,2,3-Tetraphenylcyclopropane (3a). After 1,1,*trans*-2,3-tetraphenylcyclopropane (**3a**) had been irradiated for about 7 h, irradiation was interrupted. NMR spectroscopic analyses showed that about 90% of **3a** had remained unchanged although about one-fourth of an equivalent of O_2 was consumed during the reaction. According to NMR spectroscopic analyses, dioxolanes were not formed. Instead, benzophenone and benzaldehyde in a ratio of approximately 1:1 were found besides minor amounts of other, unidentified products. Photooxygenation beyond 25% of cyclopropane consumption led to an even more complex mixture of products.

DCA- and 1,8-AQ-Photosensitized Rearrangements of *trans*-2,3-Diaryl-1,1-diphenylcyclopropanes. As described above, cyclopropanes **3f–i** rearranged to the corresponding 3,3-diaryl-1,1-diphenylpropenes **2f–i** when irradiated in oxygen- or nitrogen-saturated MeCN in the presence of DCA or 1,8-AQ as sensitizers (Scheme IV). The photosensitized rearrangements of **3f–i** represent the reverse reactions of the UV-light induced rearrangements of the 1,1,3,3-tetraarylpropenes **2f–i**. Since the latter are usually referred to as di-π-methane rearrangements, we may refer to the former as "retro-di-π-methane rearrangements", if we disregard the mechanisms involved.[22]

Discussion

We have used the well-known di-π-methane rearrangement[3] in order to synthesize 1,1,2,3-tetraarylcyclopropanes **3** from 1,1,3,3-tetraarylpropenes **2**. Of the two possible geometric isomers, only the thermodynamically more stable trans isomers **3a–i** were formed, which suffer from two eclipsed aryl–aryl interactions (one on each face of the cyclopropane ring), in contrast to the cis isomers where

three such interactions occur (on one face of the cyclopropane ring).[24]

Substitution of one or two phenyl groups of 1,1,*trans*-2,3-tetraphenylcyclopropane (**3a**) by *p*-tolyl or *p*-anisyl groups leads to two distinct kinds of tetraarylcyclopropanes: 1,1-diaryl-*trans*-2,3-diphenylcyclopropanes **3b–e** and *trans*-2,3-diaryl-1,1-diphenylcyclopropanes **3f–i**.

All these cyclopropanes, **3a–i**, proved to be inert toward singlet oxygen. This result as well as the fact that **3a–i** quench the fluorescence of DCA in MeCN with approximately diffusion-controlled rates by reducing DCA to $DCA^{\bullet-}$ in an electron-transfer process, reaction 4 (see Table I), agree very well with the results obtained with the structurally isomeric 1,1,2,2-tetraarylcyclopropanes.[1]

$$DCA + h\nu \rightarrow {}^1DCA^* \quad (3)$$

$$^1DCA^* + \mathbf{3a–i} \rightarrow DCA^{\bullet-} + (\mathbf{3a–i})^{\bullet+} \quad (4)$$

Radical cations $(\mathbf{3a–e})^{\bullet+}$ on the one hand and radical cations $(\mathbf{3f–i})^{\bullet+}$ on the other behave quite differently in their subsequent reactions. In oxygen-saturated MeCN solutions, $(\mathbf{3a–e})^{\bullet+}$ react to oxygenation products, i.e. to benzophenone and benzaldehyde as major products from $\mathbf{3a}^{\bullet+}$ and to 1,2-dioxolanes **4b–e** from $(\mathbf{3b–e})^{\bullet+}$, whereas $(\mathbf{3f–i})^{\bullet+}$ rearrange by a 1,2-aryl shift to yield finally the corresponding 3,3-diaryl-1,1-diphenylpropenes **2f–i**. Furthermore, in deoxygenated MeCN solutions, $(\mathbf{3a–e})^{\bullet+}$ experience solely a back electron transfer to **3a–e**; i.e., this process does not involve an isomerization to the corresponding 1,1-diaryl-*cis*-2,3-diphenylcyclopropanes or a rearrangement to the corresponding 1,1-diaryl-3,3-diphenylpropenes **2a–e**. Radical cations $(\mathbf{3f–i})^{\bullet+}$, however, rearrange to $(\mathbf{2f–i})^{\bullet+}$ in the same manner as in O_2-saturated solutions before they undergo a back electron transfer to afford propenes **2f–i** (Scheme IV). Back electron transfer to $(\mathbf{3f–i})^{\bullet+}$ appearently yields only the starting cyclopropanes **3f–i**, since the corresponding isomeric *cis*-2,3-diaryl-1,1-diphenylcyclopropanes were not observed.

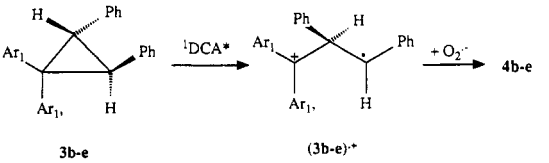
With respect to oxygenation reactions, the 1,3-radical cations of cyclopropanes **3a–e** seem to resemble those of the 1,1,2,2-cyclopropanes. There is, however, an important difference in the mechanism of the oxygenation steps. The 1,3-radical cations of 1,1,2,2-tetraarylcyclopropanes undergo 1,2-dioxolane formation in a chain reaction by using $^3O_2$,[1] whereas those of **3a–e** obviously need superoxide radical anion, $O_2^{\bullet-}$, generated by secondary electron transfer from $DCA^{\bullet-}$ to $^3O_2$, to yield oxygenation products.

$$DCA^{\bullet-} + {}^3O_2 \rightarrow DCA + O_2^{\bullet-} \quad (5)$$

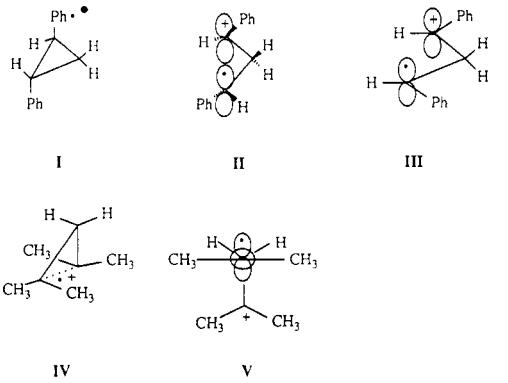
$$(\mathbf{3a–e})^{\bullet+} + O_2^{\bullet-} \rightarrow \text{oxygenation products} \quad (6)$$

This assertion is supported by the fact that small amounts of benzoquinone completely quench the DCA-photosensitized oxygenation of **3a–e** and that 1,8-AQ is incapable to sensitize the oxygenation of these cyclopropanes.[26]

Scheme V. Electron-Transfer-Induced Photooxygenation of 1,1-Diaryl-*trans*-2,3-diphenylcyclopropanes



Scheme VI. Structure of 1,3-Radical Cations Derived from *trans*-Diphenylcyclopropane[28] and 1,1,2,2-Tetramethylcyclopropane[29]



Cyclopropanes **3b–e**, bearing one or two electron-releasing aryl groups at C-1, yield 1,2-dioxolanes by ring opening exclusively between the diaryl-substituted carbon atom C-1 and the phenyl-substituted carbon atom C-2 or the phenyl-substituted carbon atom C-3 (Schemes II and III). Resonance stabilization of a positive charge is affected by electron-donor substituents to a larger extent than is that of a radical site.[27] Radical cations $(\mathbf{3b–e})^{\bullet+}$ should, therefore, bear the positive charge at C-1 and the radical electron at C-2 (Scheme V).

In the following discussion, we shall first consider the oxygenation of the (racemic) 1,1-bis(4-methylphenyl)-*trans*-2,3-diphenylcyclopropane (**3c**) and 1,1-bis(4-methoxyphenyl)-*trans*-2,3-diphenylcyclopropane (**3e**), which yield the corresponding *cis*-**4** and *trans*-**4** compounds in cis/trans ratios of 7:3 and 3:2, respectively (Scheme II).

By applying CIDNP techniques, Roth and Schilling[28] were able to show that the 1,3-radical cation derived from *trans*-1,2-diphenylcyclopropane may be represented by form II as well as by form III, in which spin and charge are delocalized. Form I, in which spin and charge are localized in one phenyl group, could be excluded (Scheme VI). Since no trans-to-cis isomerization occurred on back electron transfer, the authors identified form II with the 1,3-radical cation.

Analysis of the ESR spectra of the 1,1,2,2-tetramethylcyclopropane radical cation taken at 77 and at 117 K, enabled Williams and co-workers[29] to show that the ring-closed form IV exists at 77 K, whereas at temperatures above 110 K, the radical cation exists only in the ring-opened form V (Scheme VI).

Since we executed the irradiations at room temperature, radical cations $(\mathbf{3c,e})^{\bullet+}$ should exist in the ring-opened form VI. This conformer represents the rotamer of minimum energy, whereas conformer VII should be a rotamer of

(24) The additional strain introduced into cyclopropanes by aryl–aryl repulsion may be rather small. According to Liebman and Greenberg,[25] *cis*-1,2-diphenylcyclopropane should be less stable than *trans*-1,2-diphenylcyclopropane by no more than about 2 kcal/mol.

(25) Liebman, J. F.; Greenberg, A. In *The Chemistry of the Cyclopropyl Group*, Vol. II; Rappoport, Z., Ed.; John Wiley & Sons: New York, 1987; p 1083.

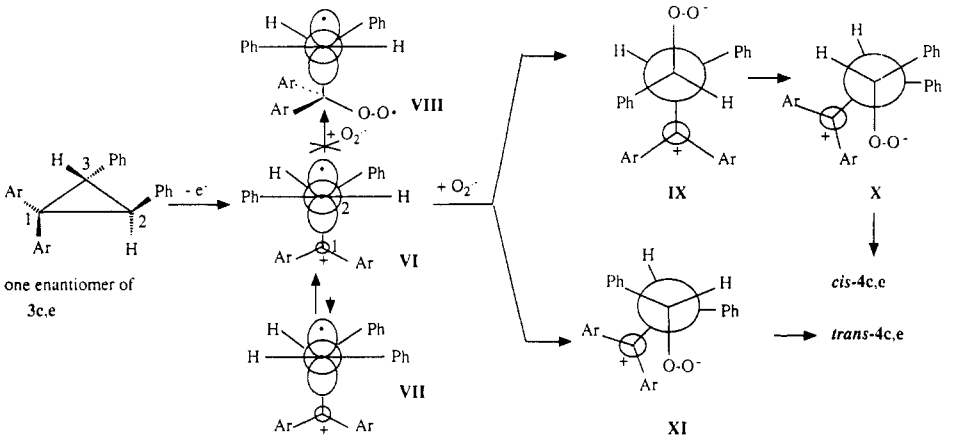
(26) The inefficiency of 1,8-AQ to act as a sensitizer is based on the fact that $(1,8\text{-AQ})^{\bullet-}$ cannot transfer an electron to $^3O_2$ (see Results Section). It is certainly not based on an inefficiency of the electronically excited 1,8-AQ to undergo an electron transfer with **3a–e** to yield $(1,8\text{-AQ})^{\bullet-} + (\mathbf{3a–e})^{\bullet+}$, since electron transfer does occur with cyclopropanes having similar oxidation potentials as, for example, cyclopropanes **3f–i** (Table III) and 1,1,2,2-tetraarylcyclopropanes.[1]

(27) Leigh, W. J.; Arnold, D. R.; Humphreys, R. W. R.; Wong, P. C. *Can. J. Chem.* **1980**, *58*, 2537 and literature cited.

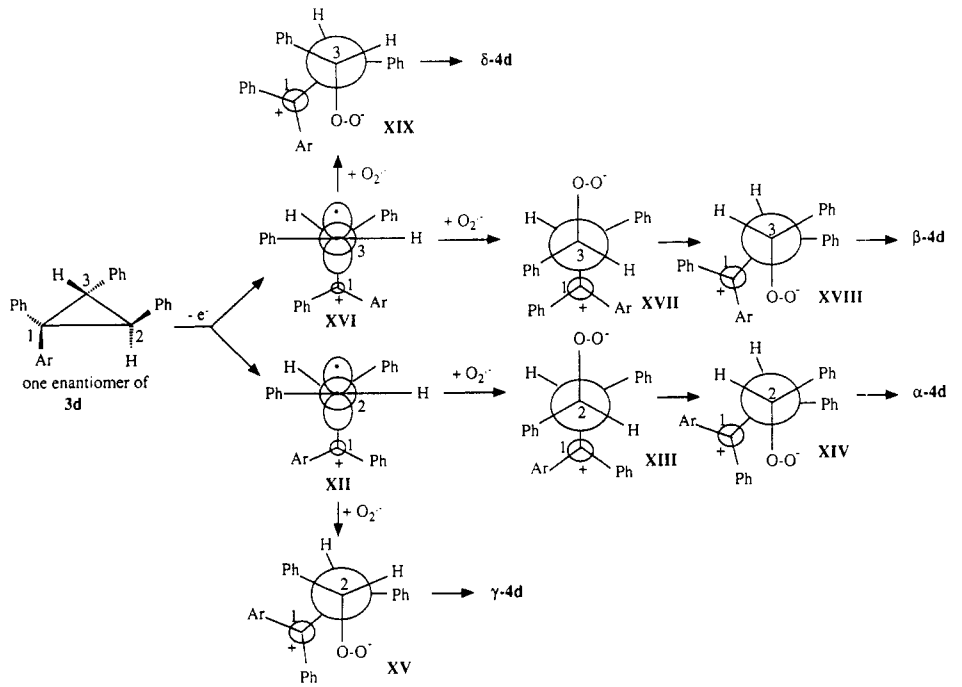
(28) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1980**, *102*, 7956.

(29) Qin, X.-Z.; Snow, L. D.; Williams, F. *J. Am. Chem. Soc.* **1984**, *106*, 7640.

Scheme VII. Formation of 1,2-Dioxolanes from 1,1-Diaryl-*trans*-2,3-diphenylcyclopropanes 3c and 3e



Scheme VIII. Formation of 1,2-Dioxolanes from *trans*-1-(4-Methoxyphenyl)-1,2,3-triphenylcyclopropane (3d)



higher energy.[30] The equilibrium should thus lie entirely on the side of conformer VI (Scheme VII).[31]

Addition of $O_2^{\bullet-}$ should thus occur exclusively to conformer VI. This addition may, in principle, proceed in a one-step cycloaddition reaction, which, however, can only occur from below the plane in which carbon atoms C-3 and C-2, the H atom at C-2, and the C atom that connects the phenyl group with C-2 are located. A concerted cycloaddition is therefore excluded from further consideration, because this mode of reaction can only give rise to the formation of *trans*-**4c** and *trans*-**4e**.

When dioxolanes **4c** and **4e** are formed in a multistep addition of $O_2^{\bullet-}$ to $(\mathbf{3c,e})^{\bullet+}$, two different paths must be considered for the first step of the addition process to conformer VI: (1) $O_2^{\bullet-}$ attack on C-1 to yield 1,5-diradical VIII; (2) $O_2^{\bullet-}$ attack on C-2 to afford 1,5-zwitterions IX and XI. In both cases, the addition may occur on either side of the p orbitals at C-1 or C-2, respectively (Scheme VII).

Let us first consider the addition of $O_2^{\bullet-}$ to C-1. No matter which lobe of the p orbital at C-1 is attacked by $O_2^{\bullet-}$, as long as we do not allow rotation about the C-2/C-3 bond, only *trans*-**4c** and *trans*-**4e** will be formed on ring closure (which requires rotation about the C-1/C-3 bond in case that the outer lobe of the C-1 p orbital is attacked).

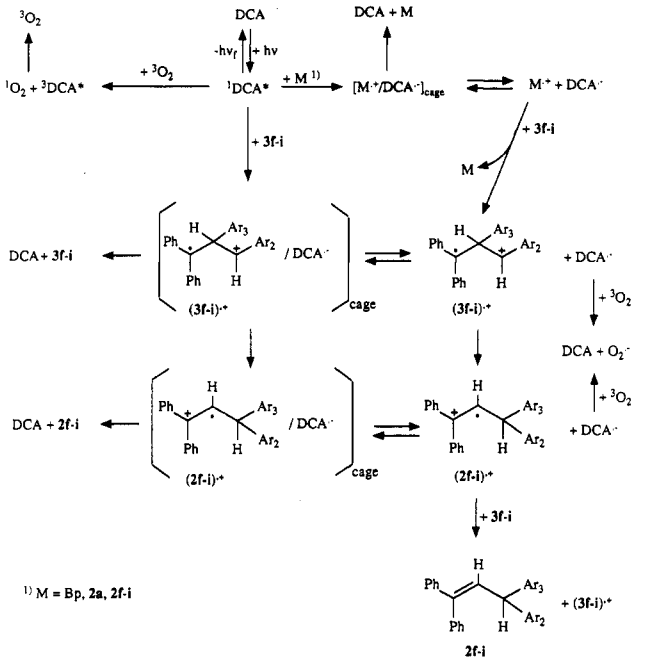
Now let us consider the addition of $O_2^{\bullet-}$ to C-2. Attack of $O_2^{\bullet-}$ from above, i.e., on the outer lobe of the p orbital at C-2 yielding IX, appears to be less sterically hindered than from below, i.e., on the inner lobe of the C-2 p orbital affording XI. In the latter case, ring closure may immediately follow (without rotation about the C-2/C-3 bond), giving rise to the minor products, *trans*-**4c** and *trans*-**4e**. In the former case, rotation about the C-2/C-3 bond of IX is necessary to give X before ring closure can take place that leads to the major products, *cis*-**4c** and *cis*-**4e**.

We therefore suggest that dioxolane formation occurs in two steps: addition of $O_2^{\bullet-}$ to the less substituted C-2 atom, preferentially from the less hindered side, affording

(30) The dihedral angle between the two phenyl groups in VII is 30°. The energy of conformer VII is thus close to the that of the fully eclipsed rotamer. VII should therefore resemble a transition state rather than a conformer of any appreciable lifetime.

(31) Note that only one enantiomer of **3c,e** is shown and that ring-opening between C-1 and C-2 is equivalent to ring-opening between C-1 and C-3. Furthermore, the cis isomers of **3c,e** (1,1-diaryl-*cis*-2,3-diphenylcyclopropanes) should also yield conformer VI by electron transfer; i.e., in contrast to **3c,e**, the cis isomers should undergo cis-to-trans isomerization on DCA photosensitization in MeCN. We are presently engaged with such studies.

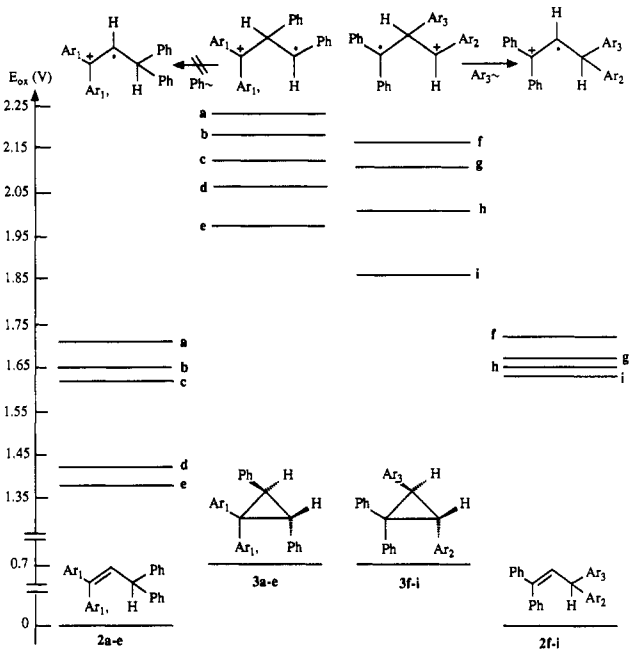
Scheme IX. Mechanism of DCA-Photosensitized Rearrangement of *trans*-2,3-Diaryl-1,1-diphenylcyclopropanes. Effects of Biphenyl, Oxygen, and Products (3,3-Diaryl-1,1-diphenylpropenes) on the Reaction Rates



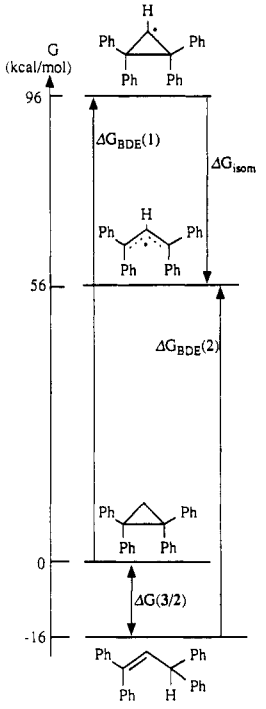
a 1,5-zwitterion, which (with or without rotation about the C-2/C-3 bond) undergoes ring closure to the observed products.

Let us now turn to the oxygenation of the (racemic) *trans*-1-(4-methoyphenyl)-1,2,3-triphenylcyclopropane (**3d**). (Dioxolane formation from *trans*-1-(4-methylphenyl)-1,2,3-triphenylcyclopropane (**3b**) will probably occur in an analogous manner.) Ring-opening between C-1 and C-2 is here not equivalent to ring-opening between C-1 and C-3. Moreover, it is necessary to assume that the rotations about the C-1/C-3 bond in XII and the C-1/C-2 bond in XVI are forbidden or at least largely restricted (Scheme VIII; note that only one enantiomer of **3d** is shown).[32] Attack of $O_2^{\bullet-}$ on the radical sites of XII and XVI from the less hindered sides yields zwitterions XIII and XVII, respectively. These zwitterions afford the major products α-**4d** and β-**4d** after rotation to XIV and XVIII followed by ring-closure. Attack of $O_2^{\bullet-}$ on the radical sites of XII and XVI from the sterically more hindered side yields the minor components γ-**4d** and δ-**4d** via XV and XIX, respectively. The isomers α-**4d**, β-**4d**, γ-**4d**, and δ-**4d** are formed in a ratio of 9:6:3:2 (Scheme III). This means that the "cis" products (α-**4d** + β-**4d**) and the "trans" products (γ-**4d** + δ-**4d**) are formed in a ratio of 3:1, which agrees well with the cis/trans ratios found for dioxolanes **4c** and **4e**.[33] Provided that the model is virtually correct,

Scheme X. Energy Levels of 1,1,3,3-Tetraarylpropenes and 1,1,*trans*-2,3-Tetraarylcyclopropanes and Their 1,3-Radical Cations



Scheme XI. Determination of $\Delta G(3/2)$



ring-opening of the C-1/C-2 bond is preferred over ring-opening of the C-1/C-3 bond, yielding XII and XVI, respectively, by a factor of 1.5; the attack of $O_2^{\bullet-}$ from the less hindered side on the radical sites of XII and XVI is preferred over that from the more hindered side by a factor of 3. (For another attempt to explain product distributions, see footnote 37).

(32) We have not yet studied these reactions with an enantiomer of **3d**. By using such an enantiomer, e.g., the one shown in Scheme VIII, back electron transfer to XII and XVI should restore this enantiomer, if rotations about the C-1/C-3 bond of XII and the C-1/C-2 bond of XVI are completely hindered; however, if they occur unhindered, the racemate should be formed.

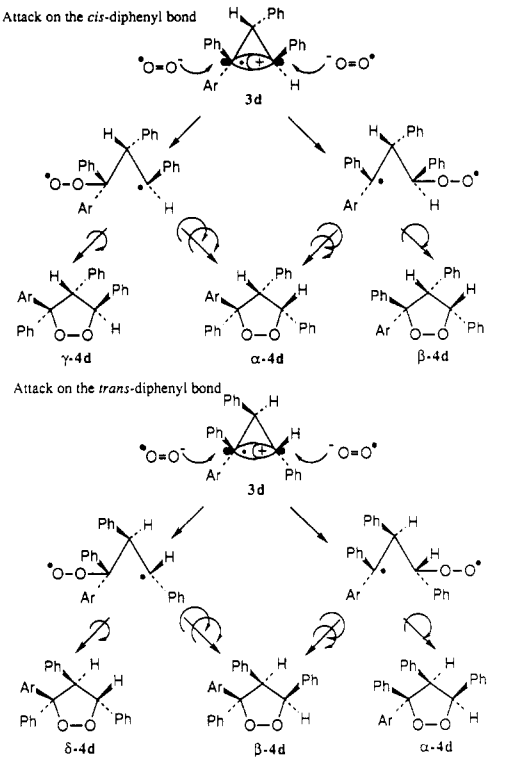
(33) It should be noted that no assumption with respect to the hindrance or nonhindrance of the rotation about the C-1/C-2 bond in VI (Scheme VII) had to be made to derive the product distribution of dioxolanes **4c** and **4e**. However, it should further be noted that the assumption of a free rotation about the C-1/C-3 bond in XII and about the C-1/C-2 bond in XVI would lead to 1:1 ratios for the formation α-**4d** and β-**4d** as well as for the formation of γ-**4d** and δ-**4d**, whereas experimentally ratios of 3:2 were obtained in each case.

(34) For reviews, see: (a) Wilt, J. W. In *Free Radicals*, Vol. I; Kochi, J. K., Ed.; John Wiley-Interscience: New York, 1973; p 333. (b) Nonhebel, D. C.; Walton, J. C. *Free-Radical Chemistry*; Cambridge University Press: Cambridge, 1974. (c) March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley: New York, 1985.

(35) Wayner, D. D. M.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 871.

As with 1,1,2,2-tetraarylcyclopropanes,[1] the course of photooxygenation becomes less plain with 1,1-diaryl-*trans*-2,3-diphenylcyclopropanes, which bear aryl groups with none (**3a**) or only one weak electron-releasing substituent (**3b**). Cyclopropane **3b** gives rise to 1,2-dioxolanes **4b**, one of which could be isolated (α-**4b** or β-**4b**). However, appreciable amounts of benzaldehyde and 4-methylbenzophenone were formed along with the dioxolanes and some other, unidentified products.

Scheme XII



Cyclopropane **3a** does not yield detectable amounts of dioxolanes; only benzaldehyde and benzophenone were obtained apart from some other, unidentified products. Considering the stability of aryl-substituted dioxolanes in general, it seems rather unlikely that the aldehydes and ketones are thermal or photochemical fragmentation products of dioxolanes. Since $O_2^{\bullet-}$ rather than $^3O_2$ is necessary for the oxygenation process, formation of the carbonyl products via allylic radicals **3a**$^\bullet$ and **3b**$^\bullet$, generated by deprotonation of the corresponding radical cations **3a**$^{\bullet+}$ and **3b**$^{\bullet+}$ (compare Scheme V of the preceding paper[1]), appears to be rather unlikely as well.

Competing with ring closure, transformation of zwitterions (**3a,b**)$^+$-**OO**$^-$ (whose structure should be similar to IX and XI, for example) to allylic hydroperoxides Ar(Ph)C=C(Ph)CH(Ph)OOH followed by photooxygenation and fragmentation of the products (compare Scheme VI of the preceding paper[1]) could explain the formation of carbonyl compounds. But this mechanism is speculative at present.

trans-2,3-Diaryl-1,1-diphenylcyclopropanes **3f–i** yield 3,3-diaryl-1,1-diphenylpropenes **2f–i** on DCA photosensitization, indicating that ring-opening occurs exclusively between C-1 and C-2 (or C-3). If, as stated above, resonance stabilization of a positive charge is affected by electron-releasing substituents to a larger extent than is the resonance stabilization of a radical site, radical cations (**3f–i**)$^{\bullet+}$ should bear the positive charge at C-2 and the radical site at C-1 (Scheme IX). These radical cations suffer a 1,2-aryl shift, presumably to some extent in the primary cage before back electron transfer takes place, and certainly in a fast and efficient way when outside this cage as a "free" radical cation. The latter conclusion is drawn from the fact that biphenyl as well as O_2 enhance the propene formation appreciably. Biphenyl generates "free" (**3f–i**)$^{\bullet+}$ in a secondary electron-transfer process, whereas O_2 traps DCA$^{\bullet-}$ (reaction 5), thus enhancing the concen-

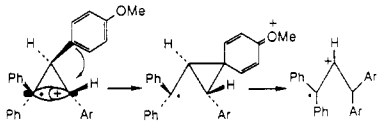
(36) (a) Gollnick, K.; Schnatterer, A. *Tetrahedron Lett.* **1984**, *25*, 185. (b) Gollnick, K.; Schnatterer, A. *Tetrahedron Lett.* **1984**, *25*, 2735. (c) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1986**, *108*, 7356.

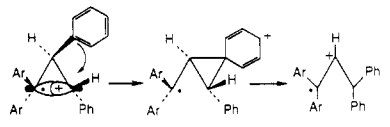
(37) A referee suggested that, compared with 1,1,2,3-tetraarylcyclopropanes, in 1,1,2,2-tetraarylcyclopropanes the additional aryl group will restrict the radical cation (hole) to a single cyclopropane bond (between C-1 and C-2), weaken that bond more effectively, and make the formation of the open radical cation likely. The so-formed 1,3-radical cation is then attacked by triplet oxygen (see preceding paper[1]).

The hole in the 1,1,2,3-tetraarylcyclopropanes, on the other hand, will be more or less delocalized between two cyclopropane bonds, as indicated in Scheme XII, leading to less effective weakening of the individual cyclopropane bonds and thus tending to favor the closed radical cation. The latter will probably be less susceptible to nucleophilic attack by the much better nucleophilic superoxide ion. This mechanism will lead to the same isomers of compound **4** with statistics consistent with the experimental observations.

The assumption of closed radical cations would also account for the fact that on back electron transfer to **3d**$^{\bullet+}$, no isomerization is observed.

Furthermore, intramolecular nucleophilic attack by a *p*-methoxyphenyl group would account for the rearrangement of the *trans*-2,3-bis(4-methoxyphenyl)-1,1-diphenylcyclopropane (**3i**) as shown:





In contrast, the less nucleophilic phenyl groups of the 1,1-bis(4-methoxyphenyl)-*trans*-2,3-diphenylcyclopropane (**3e**) might not be powerful enough nucleophiles to induce ring cleavage, and thus, this radical cation could survive to react with a more powerful external nucleophile such as superoxide ion.

In our opinion, there are some observations that disagree with the above mechanistic explanations. (a) If 1,1,2,2-tetraaryl substitution is necessary to produce an open cyclopropane radical cation, one should expect 1,2-diarylcyclopropanes to form closed radical cations, which, consequently, should react with superoxide ion rather than with triplet oxygen. According to Mizuno et al.,[15] however, dioxolanes from *trans*-1,2-diarylcyclopropanes are formed via reactions with triplet oxygen. We have repeated Mizuno's experiments with *trans*-1-(4-methoxyphenyl)-2-phenylcyclopropane and with *trans*-1,2-bis(4-methoxyphenyl)cyclopropane using DCA as a sensitizer and *p*-benzoquinone as a superoxide ion quencher as well as with 1,8-AQ as a sensitizer. Since *p*-benzoquinone does not effect dioxolane formation and 1,8-AQ acts as a sensitizer, these observations strongly support Mizuno's results. Thus, open radical cations should be formed, which, according to the referee's suggestion, should undergo isomerization (here to the corresponding *cis*-1,2-diarylcyclopropanes) on back electron transfer. This, however, is not the case.[15,28] (b) The radical cation derived from 1,2-*cis*-bis(4-methoxyphenyl)cyclopropane, on the other hand, does undergo isomerization to the trans compound.[15] Similarly, the radical cation derived from *all-cis*-1,2,3-triphenylcyclopropane yields the cis–trans isomer on back electron transfer (Gollnick, K.; Paulmann, U., unpublished results). Thus, open 1,3-radical cations obviously tend to form the thermodynamically more favorable cyclopropanes on back electron transfer. An explanation for this result is presented in Scheme VII (equilibrium between radical cations VI and VII almost completely in favor of VI) and footnote 30 (see also footnote 31). (c) In *trans*-2-(4-methoxyphenyl)-1,1,3-triphenylcyclopropane (**3h**), the σ-bonds C-1/C-2 and C-1/C-3 are not equivalent. If **3h**$^{\bullet+}$ were a closed radical cation, the single electron bond should be expected to be located between C-1 and C-2 rather than between C-1 and C-3. In this case, **3h**$^{\bullet+}$ would bear a poor nucleophilic phenyl group at C-3 and, thus, no rearrangement to **2h** should take place. Instead, dioxolane formation should occur. If one assumes some delocalization of the hole in **3h**$^{\bullet+}$, one might still expect dioxolane formation to occur besides some rearrangement to **2h**.

We feel that the reasons for the preference of aryl-substituted cyclopropane radical cations for either $^3O_2$ or $O_2^{\bullet-}$ remain still to be elucidated.

tration of the "free" radical cations. Since we do not observe any dioxolane formation, 1,3-radical cations $(3f-i)^{\bullet+}$ are either incapable of reacting with $O_2^{\bullet-}$ and $^3O_2$ or they rearrange too fast to the corresponding 1,2-radical cations $(2f-i)^{\bullet+}$ to give the bimolecular dioxolane formation a chance to occur. The comparatively slow reaction of 1,2-radical cations $2^{\bullet+}$ with $O_2^{\bullet-}$ are known from our previous studies.[1] Because propenes **2f–i** have higher oxidation potentials than the corresponding cyclopropanes **3f–i**, radical cations $(2f-i)^{\bullet+}$ abstract readily an electron from the starting cyclopropane, thus inducing a chain reaction and, simultaneously, increasing the concentration of "free" radical cations $(3f-i)^{\bullet+}$ when the electron-transfer-induced rearrangement of the cyclopropanes proceeds. In accord with this assertion is the fact that added propene **2a** serves this purpose as well (Table III). In other words, whereas the rearrangement products **2f–i** act as co-sensitizers for the rearrangement of cyclopropanes **3f–i**, these cyclopropanes act as quenchers for the electron-transfer-induced oxygenation of propenes **2f–i**.

It is a well-established fact that 1,2-aryl shifts to a carbon cation occurs much more readily than to a carbon radical site, because the polar reaction may proceed via a phenonium ion intermediate, whereas a corresponding bridged radical represents only a transition state.[34] We therefore assume that rearrangements of $(3f-i)^{\bullet+}$ occur fast and efficiently because their transformations proceed via phenonium ion intermediates. $(3a-e)^{\bullet+}$ could rearrange to the corresponding 1,2-radical cations $(2a-e)^{\bullet+}$ only via 1,2-aryl shifts to a radical site, which, however, are obviously too slow to compete with the oxygenation reactions.

This assertion is substantiated by the fact that, with regard to free enthalpy changes, both the polar as well as the radical pathway of the 1,2-aryl shift should be possible (Scheme X).

By using the C–H bond dissociation energies $\Delta G_{BDE}(1)$ = 96 kcal mol^{-1} for 1,1,2,2-tetraphenylcyclopropane and $\Delta G_{BDE}(2)$ = 72 kcal mol^{-1} for 1,1,3,3-tetraphenylpropene (**2a**), and the isomerization energy ΔG_{isom} = −39 kcal mol^{-1},[35] we find that the propene derivative is more stable than the cyclopropane derivative by $\Delta G(3/2)$ = −16 kcal mol^{-1} (= −0.7 eV) (Scheme XI). Since 1,1,*trans*-2,3-tetraphenylcyclopropane (**3a**) suffers from one phenyl–phenyl repulsion on each face of the cyclopropane ring as does 1,1,2,2-tetraphenylcyclopropane, we assume that the energy differences between **2a** and the two tetraphenylcyclopropanes are approximately the same. Moreover, if $\Delta G_{BDE}(1)$ is independent of the aryl substituents at C-1 and C-2 (Scheme XI), the energy gain in ΔG_{isom} (for example, by replacing one phenyl group by a 4-methoxyphenyl group) may approximately be compensated by the energy loss in $\Delta G_{BDE}(2)$, thus leaving the energy differences between the tetraarylcyclopropanes and the tetraarylpropenes nearly untouched. With these assumptions, the energy levels of radical cations $(2a-i)^{\bullet+}$ and $(3a-i)^{\bullet+}$ in acetonitrile (Scheme X) were calculated.

Conclusion

Rates and products of electron-transfer-induced reactions of 1,1,*trans*-2,3-tetraarylcyclopropanes **3**, bearing phenyl, *p*-tolyl, and *p*-anisyl groups as aryl substituents, are governed by the structure and resonance stabilization of the cationic site of the 1,3-radical cations formed. In deoxygenated acetonitrile, the 1,3-radical cations of 1,1-diaryl-*trans*-2,3-diphenylcyclopropanes and of 1,1,*trans*-2,3-tetraphenylcyclopropane, $(3a-e)^{\bullet+}$, bearing the cationic site at C-1, yield the starting material on back electron transfer, whereas in oxygenated acetonitrile, they react with superoxide radical anions, $O_2^{\bullet-}$, to oxygenated products. 1,3-Radical ions of *trans*-2,3-diaryl-1,1-diphenylcyclopropanes, $(3f-i)^{\bullet+}$, bearing the cationic site at C-2, undergo either back electron transfer to starting material or a 1,2-aryl migration that finally leads to 3,3-diaryl-1,1-diphenylpropenes **2f–i**. Remarkably enough, the rearrangement occurs not only in deoxygenated but also in oxygen-saturated acetonitrile solutions. Another remarkable result is the fact that none of the radical cations $(3a-i)^{\bullet+}$ undergoes an isomerization to the corresponding 1,1,*cis*-2,3-tetraarylcyclopropane on back electron transfer. Furthermore, whereas the dioxolane formation from 1,3-radical cations derived from 1,1,2,2-tetraarylcyclopropanes requires $^3O_2$, that from $(3a-e)^{\bullet+}$ requires $O_2^{\bullet-}$. Although we have no explanation ready at hand for this different behavior, we may state a certain tendency in reactivity of radical cations toward $^3O_2$ and $O_2^{\bullet-}$. Thus, 1,2-radical cations, having the radical electron and the positive charge in two adjacent p orbitals, prefer to react with superoxide radical anions,[8] whereas 1,4-radical cations, having the radical electron and the positive charge in p orbitals that are separated by two sp^3 carbon atoms, prefer to react with triplet ground-state oxygen.[36] 1,3-Radicals, derived from cyclopropanes, obviously represent an intermediate case; they bear the radical electron and the positive charge in two p orbitals, which, though separated by one sp^3 carbon atom, may interact with each other to some extent (an extreme form being the one-electron bond in form II of Scheme VI). The reasons for the preference of 1,3-radical cations for either $^3O_2$[1,15] or $O_2^{\bullet-}$ remain to be elucidated.[37]

Experimental Section

Solvents and commercially available compounds were purchased from standard suppliers and purified to match reported physical constants and spectral data. Special care was taken to obtain pure and dry MeCN; acetonitrile (Merck, Darmstadt, p.a.) was therefore distilled over P_2O_5 and K_2CO_3 in sequence. 9,10-Dicyanoanthracene, mp 346–347 °C, was prepared according to the method of Beyer and Fritsch.[38] Other known compounds were prepared according to literature procedures and used (such as the 1,3,3-triarylpropanones **1a–i**) after appropriate purifications. Melting points are uncorrected.

UV spectra were recorded on a Zeiss RPQ 20C spectrometer. IR spectra were taken on a Bruker IFS 45 instrument either in Nujol or KBr or as thin films. ^{1}H NMR spectra were recorded on a Bruker WP-80 and a Varian XL 100 spectrometer with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. ^{13}C NMR spectra were recorded at 22.3 MHz on a Bruker WP-80 spectrometer with $CDCl_3$ as solvent and TMS as internal standard. Mass spectra were taken at 70 eV on an AEI mass spectrometer MS 902.

The purity of compounds **2c**, (α- or β)-**4b**, and the mixture of (α-**4d** + β-**4d**) were judged to be ≥90% by ^{1}H and/or ^{13}C NMR spectral determinations. The spectra are found in the supplementary material.

Fluorescence quenching of deoxygenated MeCN solutions of DCA (2×10^{-5} M) was executed on a Zeiss-4C fluorescence spectrometer equipped with a Xe lamp XBO 450 W. Excitation of DCA was carried out at 383 nm, and the fluorescence intensities were determined at 450 nm, i.e., at the first minimum of the DCA fluorescence spectrum. The quenchers (**3a–i**) were used at at least six different concentrations between 0.002 and 0.03 M.

Redox potentials were measured by cyclic voltammetry on a cyclic voltammograph CV-1B (Bioanalytical Systems, Inc.) at a platinum electrode vs the standard calomel electrode (SCE) in Ar-saturated MeCN. The supporting electrolyte was tetraethylammonium tetrafluoroborate (0.1 M); scan speed 400 mV/s. The instrument was calibrated by using 1,3,5-trimethoxybenzene as a standard.

Preparation of 1,1,3,3-Tetraarylpropenes. General Procedure. The Grignard reagents Ar_1MgBr were prepared from

(38) Beyer, H.; Fritsch, H. *Ber. Dtsch. Chem. Ges.* **1941**, *74*, 494.

Mg in dry ether and bromobenzene (PhMgBr), *p*-bromoanisol (AnMgBr), and *p*-bromotoluene (TolMgBr). To the Grignard solution was added a suspension of the appropriate 1,3,3-triaryl-1-propanone 1 in dry ether slowly at 0 °C. The mixture was refluxed for 2 h and then treated with 2 N HCl. The organic layer was extracted with ether; the latter was subsequently dried over magnesium sulfate. After removal of the ether, the oily carbinol was solved in acetic acid. A few drops of concentrated sulfuric acid were added and the solution heated to about 80 °C for 3 h. The hot solution was poured on ice, and the product was subsequently solved in ether. After drying over $MgSO_4$ and removal of the ether, the oily 1,1,3,3-tetraarylpropene **2** was recrystallized from ethanol.

1,1,3,3-Tetraphenylpropene (2a). PhMgBr (0.06 mol) and 15.0 g (0.05 mol) of 1,3,3-triphenyl-1-propanone (**1a**) gave 5.5 g of **2a** (colorless needles; yield: 30%), mp 126–127 °C (lit.[39] mp 127 °C). ^1H NMR: δ 4.76 (d, 1 H, J = 11.2 Hz), 6.48 (d, 1 H, J = 11.2 Hz), 7.16 (m, 20 H, Ar).

(*E*,*Z*)-1-(4-Methylphenyl)-1,3,3-triphenylpropene (2b). PhMgBr (0.1 mol) and 15.0 g (0.050 mol) of 3,3-diphenyl-1-(4-methylphenyl)-1-propanone (**1b**, mp 96–97 °C) afforded 11.9 g of **2b** (colorless crystals; yield 66%), mp 103–104 °C. ^1H NMR: δ 2.28 and 2.32 (s, 3 H, CH_3), 4.78 and 4.83 (d, 1 H, J = 10 Hz), 6.50 (d, 1 H, J = 10 Hz), 7.18 (m, 18 H, Ar).

Anal. Calcd for $C_{28}H_{24}$ (360.47): C, 93.29; H, 6.71. Found: C, 93.43; H, 6.86.

1,1-Bis(4-methylphenyl)-3,3-diphenylpropene (2c). TolMgBr (0.1 mol) and 15.0 g (0.050 mol) of 3,3-diphenyl-1-(4-methylphenyl)-1-propanone (**1c** = **1b**) yielded 15.0 g of **2c** (as a yellowish oil after chromatography over alumina (40-cm column); yield 80%). ^1H NMR: δ 2.25 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 4.80 (d, 1 H, J = 11 Hz), 6.42 (d, 1 H, J = 11 Hz), 6.83–7.27 (m, 18 H, Ar).

(*E*,*Z*)-1-(4-Methoxyphenyl)-1,3,3-triphenylpropene (2d). PhMgBr (0.2 mol) and 23.0 g (0.074 mol) of 3,3-diphenyl-1-(4-methoxyphenyl)-1-propanone (**1d**, mp 103–104 °C), prepared according to the method of ref 40, yielded 14.6 g of **2d** (colorless crystals, yield 52%), mp 91 °C. ^1H NMR: δ 3.74 (s, 3 H, OCH_3), 4.75 (d, 1 H, J = 10 Hz), 6.42 (d, 1 H, J = 10 Hz), 6.66–7.32 (m, 19 H, Ar).

Anal. Calcd for $C_{28}H_{24}O$ (376.47): C, 89.32; H, 6.43. Found: C, 88.97; H, 6.39.

1,1-Bis(4-methoxyphenyl)-3,3-diphenylpropene (2e). AnMgBr (0.2 mol) and 25.0 g (0.079 mol) of 3,3-diphenyl-1-(4-methoxyphenyl)-1-propanone (**1e** = **1d**) afforded 10.5 g of **2e** (colorless crystals, yield 35%), mp 82–84 °C (lit.[41] mp 86–88 °C). ^1H NMR: δ 3.72 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH_3), 4.80 (d, 1 H, J = 10 Hz), 6.37 (d, 1 H, J = 10 Hz), 6.54–7.21 (m, 18 H, Ar).

3-(4-Methylphenyl)-1,1,3-triphenylpropene (2f). PhMgBr (0.1 mol) and 15.0 g (0.05 mol) of 1,3-diphenyl-3-(4-methylphenyl)-1-propanone gave 12.7 g of **2f** (colorless crystals; yield 70%), mp 99–100 °C. ^1H NMR: δ 2.28 (s, 3 H, CH_3), 4.78 (d, 1 H, J = 10 Hz), 6.51 (d, 1 H, J = 10 Hz), 7.01–7.30 (m, 18 H, Ar).

Anal. Calcd for $C_{28}H_{24}$ (360.47): C, 93.29; H, 6.71. Found: C, 93.45; H, 6.64.

3,3-Bis(4-methylphenyl)-1,1-diphenylpropene (2g). PhMgBr (0.1 mol) and 15.7 g (0.050 mol) of 3,3-bis(4-methylphenyl)-1-phenyl-1-propanone (**1g**, mp 96–97 °C), prepared according to the method of ref 42, gave 16.0 g of **2g** (colorless crystals, yield 85%), mp 139–140 °C. ^1H NMR: δ 2.25 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 4.71 (d, 1 H, 11 Hz), 6.41 (d, 1 H, J = 11 Hz), 7.01–7.27 (m, 18 H, Ar).

Anal. Calcd for $C_{29}H_{26}$ (374.50): C, 93.00; H, 7.00. Found: C, 93.24; H, 6.97.

3-(4-Methoxyphenyl)-1,1,3-triphenylpropene (2h). PhMgBr (0.2 mol) and 23.0 g (0.074 mol) of 1,3-diphenyl-3-(4-methoxyphenyl)-1-propanone (**1h**, mp 92 °C), prepared according to the method of ref 40, afforded 13.9 g of **2h** (colorless crystals; yield 50%), mp 74 °C. ^1H NMR: δ 3.71 (s, 3 H, OCH_3), 4.73 (d, 1 H, J = 10 Hz), 6.47 (d, 1 H, J = 10 Hz), 6.70–7.36 (m, 19 H, Ar).

Anal. Calcd for $C_{28}H_{24}O$ (376.47): C, 89.32; H, 6.43. Found: C, 89.61; H, 6.42.

3,3-Bis(4-methoxyphenyl)-1,1-diphenylpropene (2i). PhMgBr (0.2 mol) and 24.3 g (0.070 mol) of 3,3-bis(4-methoxyphenyl)-1-phenyl-1-propanone (**1i**, mp 104–105 °C) gave 16.2 g of **2i** (colorless needles, yield 57%), mp 93–94 °C. ^1H NMR: δ 3.77 (s, 6 H, 2 OCH_3), 4.69 (d, 1 H, J = 11 Hz), 6.44 (d, 1 H, J = 11 Hz), 6.71–7.27 (m, 18 H, Ar).

Anal. Calcd for $C_{29}H_{26}O_2$ (406.50): C, 85.68; H, 6.45. Found: C, 85.98; H. 6.38.

Di-π-methane Rearrangements of 1,1,3,3-Tetraarylpropenes 2a–i. Preparation of 1,1,2,3-Tetraarylcyclopropanes 3a–i. General Procedure. Irradiations of 150 mL of dry benzene solutions containing about 0.015 mol of the respective 1,1,3,3-tetraaryl-1-propene were carried out in an immersion-type irradiation vessel equipped with a mercury high pressure lamp (Philips, HP 125 W) surrounded by a quartz water jacket. All reactions were run under dry nitrogen, and all solutions were purged with oxygen-free nitrogen for 1 h prior to and during the photochemical reaction. Irradiations, performed at 13 °C, lasted for about 20 h to several days to obtain the respective cyclopropanes in yields better than 50%. The workup procedure consisted of removal of benzene followed by chromatography of the oily product on alumina (50-cm column) with fresh benzene and recrystallization of the colorless crystals from ethanol.

1,1,*trans*-2,3-Tetraphenylcyclopropane (3a). After 20 h, 5.5 g (0.016 mol) of **2a** yielded 2.9 g (53%) of **3a**, mp 130–131 °C (lit.[4] mp 130–131 °C). ^1H NMR: δ 3.42 (s, 2 H), 6.82–7.25 (m, 20 H, Ar). ^{13}C NMR: δ 35.6 (d), 48.3 (s). UV (CH_2Cl_2): λ_{max} = 226 nm (log ϵ = 4.50).

1-(4-Methylphenyl)-1,*trans*-2,3-triphenylcyclopropane (3b). After 20 h, 5.4 g (0.015 mol) of **2b** gave 2.7 g (50%) of **3b**, mp 143–144 °C. ^1H NMR: δ 2.18 (s, 3 H, CH_3), 3.40 (s, 2 H), 7.20 (m, 19 H, Ar). ^{13}C NMR: δ 20.9 (q), 35.7 (2 d), 48.1 (s).

Anal. Calcd for $C_{28}H_{24}$ (360.47): C, 93.29; H, 6.71. Found: C, 93.49; H, 6.70.

1,1-Bis(4-methylphenyl)-*trans*-2,3-diphenylcyclopropane (3c). After 20 h, 18.0 g (0.048 mol) of **2c** yielded 8.6 g (48%) of **3c**, mp 199–201 °C. ^1H NMR: δ 2.18 (s, 6 H, 2 CH_3), 3.39 (s, 2 H), 6.80–7.11 (m, 18 H, Ar). ^{13}C NMR: δ 21.0 (q), 35.8 (d), 47.8 (s). UV (CH_2Cl_2): λ_{max} = 230 nm (log ϵ = 4.47); shoulders at λ = 265 nm (log ϵ = 3.31) and 275 nm (log ϵ = 3.13).

Anal. Calcd for $C_{29}H_{26}$ (374.50): C, 93.00; H, 7.00. Found: C, 92.88; H, 7.04.

1-(4-Methoxyphenyl)-1,*trans*-2,3-triphenylcyclopropane (3d). After 24 h, 5.6 g (0.015 mol) of **2d** gave 3.1 g (55%) of **3d**, mp 125–126 °C. ^1H NMR: δ 3.41 (s, 2 H), 3.65 (s, 3 H, OCH_3), 6.55–7.17 (m, 19 H, Ar). ^{13}C NMR: δ 35.6 (d), 35.9 (d), 47.6 (s), 54.6 (q). UV (CH_2Cl_2): λ_{max} = 228 nm (log ϵ = 4.45); shoulders at λ = 274 nm (log ϵ = 3.30); 285 nm (log ϵ = 3.13).

Anal. Calcd for $C_{28}H_{24}O$ (376.47): C, 89.32; H, 6.43. Found: C, 89.63; H, 6.29.

1,1-Bis(4-methoxyphenyl)-*trans*-2,3-diphenylcyclopropane (3e). After 7 days, 6.1 g (0.015 mol) of **2e** yielded 3.1 g (51%) of **3e**, mp 153–154 °C. ^1H NMR: δ 3.33 (s, 2 H), 3.66 (s, 6 H, 2 OCH_3), 6.54–7.10 (m, 18 H, Ar). ^{13}C NMR: δ 35.9 (d), 47.0 (s), 55.0 (q). UV (CH_2Cl_2): λ_{max} = 275 nm (log ϵ = 3.55); shoulder at λ = 285 nm (log ϵ = 3.40). MS (70 eV): m/e = 406.

Anal. Calcd for $C_{29}H_{26}O_2$ (406.50): C, 85.68; H, 6.45. Found: C, 85.49; H, 6.50.

Procedure for Single-Crystal X-ray Structure Determination. X-ray data were collected on an ENRAF-Nonius CAD4 diffractometer (Table IV). Unit cell parameters were determined by least-squares refinement of 25 reflections. Data were collected with 3 check reflections being monitored after every 100, and data having $I < 2\sigma(I)$ were rejected. Lorentz and polarization corrections were applied, and the structure was solved under appropriate space group symmetry by direct methods using MULTAN80[43] and refined by SHELXTL-PLUS.[44] Hydrogen atoms were located as riding atoms, and full matrix least-square refinement

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Table IV. Summary of Crystal Data Collection Parameters for 3e

a axis, Å	10.133 (2)
b axis, Å	14.426 (3)
c axis, Å	15.402 (3)
α angle, deg	90.00 (2)
β angle, deg	90.37 (2)
γ angle, deg	90.00 (2)
D_{calc} (g cm^{-3})	1.201
molecules/cell (Z)	4
space group	$P2_1/n$ No. 14
μ, cm^{-1}	0.454
radiation type	Mo Kα
scan mode	ω
2θ limits, deg	4.0–50
scan range, deg	0.90 + 0.35 tan θ
measured reflexions	4290
unique reflexions	3088
observed reflexions	2318
R_1(F)	0.0491
R_w(F)	0.0381
max. rest electron density	+0.16/−0.21 e/Å^3

was carried out employing anisotropical thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms.

***trans*-2-(4-Methylphenyl)-1,1,3-triphenylcyclopropane (3f).** After 20 h, 5.4 g (0.015 mol) of **2f** afforded 3.9 g (72%) of **3f**, mp 75–84 °C. ^{1}H NMR: δ 2.20 (s, 3 H, CH_3), 3.40 (s, 2 H), 7.20 (m, 19 H, Ar). ^{13}C NMR: δ 20.9 (q), 35.4 (d), 35.7 (d), 48.2 (s). UV (MeCN): λ_{max} = 225 nm (log ϵ = 3.79).

Anal. Calcd for $C_{28}H_{24}$ (360.47): C, 93.29; H, 6.71. Found: C, 93.60; H, 6.71.

***trans*-2,3-Bis(4-methylphenyl)-1,1-diphenylcyclopropane (3g).** After 24 h, 11.2 g (0.030 mol) of **2g** afforded 8.7 g (78%) of **3g**, mp 100–102 °C. ^{1}H NMR: δ 2.22 (s, 6 H, 2 CH_3), 3.35 (s, 2 H), 6.88–7.18 (m, 18 H, Ar). ^{13}C NMR: δ 20.9 (q), 35.4 (d), 48.0 (s). UV (CH_2Cl_2): λ_{max} = 227 nm (log ϵ = 4.42), shoulder at 255 nm (log ϵ = 4.04). MS (70 eV): m/e = 374.

Anal. Calcd for $C_{29}H_{26}$ (374.50): C, 93.00; H, 7.00. Found: C, 93.11; H, 7.05.

***trans*-2-(4-Methoxyphenyl)-1,1,3-triphenylcyclopropane (3h).** After 24 h, 5.6 g (0.015 mol) of **2h** afforded 2.9 g (53%) of **3h**, mp 121–122 °C. ^{1}H NMR: δ 3.37 (s, 2 H), 3.68 (s, 3 H, OCH_3), 6.57–7.16 (m, 19 H, Ar). ^{13}C NMR: δ 34.9 (d), 35.6 (d), 47.9 (s), 54.9 (q). UV (CH_2Cl_2): λ_{max} = 227 nm (log ϵ = 4.46), shoulder at λ = 280 nm (log ϵ = 3.28).

Anal. Calcd for $C_{28}H_{24}O$ (376.50): C, 89.33; H, 6.43. Found: C, 88.92; H, 6.50.

***trans*-2,3-Bis(4-methoxyphenyl)-1,1-diphenylcyclopropane (3i).** After 20 h, 10.3 g (0.025 mol) of **2i** afforded 6.5 g (63%) of **3i**, mp 111–112 °C. ^{1}H NMR: δ 3.33 (s, 2 H), 3.69 (s, 6 H, 2 OCH_3), 6.60–7.19 (m, 18 H, Ar). ^{13}C NMR: δ 35.0 (d), 47.5 (s), 55.0 (q). UV (CH_2Cl_2): λ_{max} = 233 nm (log ϵ = 4.42) and 282 nm (log ϵ = 3.54); shoulder at λ 274 nm (log ϵ = 3.50). MS (70 eV): m/e = 406.

Anal. Calcd for $C_{29}H_{26}O_2$ (406.50): C, 85.68; H, 6.45. Found: C, 85.76; H, 6.50.

Photooxygenations and Photorearrangements of 1,1,-*trans*-2,3-Tetraarylcyclopropanes. General Procedure for Analytical and Kinetic Runs. A 25-mL irradiation unit with automatic O_2 consumption recording system[45] was used for oxygen-uptake studies (O_2 uptake vs irradiation time) in the presence of various sensitizers and additives. Oxygen was bubbled through the solutions for 15 min before the irradiation cell was connected with the O_2-containing burette to obtain oxygen-saturated solutions. A mercury high pressure lamp HP 125 W (Philips) was used as a light source. A filter solution was placed between the lamp and the cell to cut-off wavelengths shorter than 405 nm. The filter solution was prepared from 2.3 g of $CuSO_4 \cdot 5H_2O$, 3.0 g of $NaNO_2$, and 5 mL of concentrated ammonia diluted with distilled water to 100 mL. The same irradiation cell, light source, and filter solutions were applied for irradiations of deoxygenated solutions. In this case, the cell was disconnected from the oxygen burette and the recording system, and the solutions were saturated with oxygen-free nitrogen by passing N_2 through the solutions for 15 min before irradiations were commenced. Samples were drawn from time to time and analyzed by their ^{1}H NMR spectra to determine the decrease of the starting cyclopropanes and to determine products and product distributions during irradiations of the oxygen-saturated as well as of the nitrogen-saturated solutions. The results are given in Tables II and III.

Photooxygenation of 1,1,*trans*-2,3-Tetraarylcyclopropanes. General Procedure for Preparative Runs. For preparative purposes, irradiations of 200 mL of oxygen-saturated MeCN solutions containing various amounts of the respective 1,1,2,3-tetraarylcyclopropane were carried out in an immersion-type irradiation vessel equipped with a mercury high pressure lamp (Philips, HP 125 W) surrounded by a glass water-jacket and another jacket of 1 cm width for a filter solution. The reactions were run in the presence of DCA (9.1 mg, 2 × 10^{-4} M) and under oxygen bubbling, which provided for a constant oxygen concentration and, at the same time, for vigorous stirring of the solution. A filter solution was applied that was prepared from 5.6 g of $CuSO_4 \cdot 5H_2O$, 6.0 g of $NaNO_2$, and 10 mL of concentrated ammonia diluted with distilled water to 200 mL, to cut-off wavelengths shorter than 405 nm. The reaction solutions were kept at 13 °C during the photooxygenation reactions. The progress of the reactions was followed by ^{1}H NMR analysis of samples drawn during the irradiations.

After more than 95% of the starting cyclopropane had disappeared, irradiations were stopped. After removal of MeCN at a rotatory evaporator, the oily products were solved in 25 mL of hot ethanol or n-hexane. During cooling the solutions to room temperature, DCA precipitated and was filtered off. After 1–3 days at room temperature, the 1,2-dioxolanes precipitated from the solutions, either as crystals or gels.

3-(4-Methylphenyl)-3,4,5-triphenyl-1,2-dioxolanes (4b). 1-(4-Methylphenyl)-1,*trans*-2,3-triphenylcyclopropane (**3b**) (3.60 g, 10 mmol) and 1.5 g (10 mmol) of biphenyl were oxygenated to better than 95% within 2 h. After removal of the solvent and chromatography (basic alumina, 40-cm column; elution with toluene), the residue was recrystallized from ethanol, yielding **3-(4-methylphenyl)-3,*cis*-4,5-triphenyl-1,2-dioxolane** (α-**4b** or β-**4b**) mp 81–86 °C. ^{1}H NMR: δ 2.13 (s, 3 H, CH_3), 4.75 (d, 1 H, J = 6 Hz), 5.56 (d, 1 H, J = 6 Hz), 6.83–7.20 (m, 19 H, Ar). ^{13}C NMR: δ 20.9 (q), 68.2 (d, C-4), 85.6 (d, C-5), 93.6 (s, C-3).

The ^{1}H NMR spectrum of the original solution showed the presence of about 60% of benzaldehyde and 4-methylbenzophenone (methyl protons at δ 2.35) and of about 40% of dioxolanes with methyl protons at 2.13 and between δ 2.2 and 2.4.

3,3-Bis(4-methylphenyl)-4,5-diphenyl-1,2-dioxolanes (4c). 1,1-Bis(4-methylphenyl)-*trans*-2,3-diphenylcyclopropane (**3c**) (1.0 g, 2.7 mmol) was oxygenated to better than 95% within 20 h. The workup procedure gave 0.14 g of **3,3-bis(4-methylphenyl)-*cis*-4,5-diphenyl-1,2-dioxolane (*cis*-4c)** (12%, colorless needles from n-hexane), mp 123–124 °C. ^{1}H NMR: δ 2.10 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 4.75 (d, 1 H, J = 6 Hz), 5.59 (d, 1 H, J = 6 Hz), 6.71–7.52 (m, 18 H, Ar). UV (CH_2Cl_2): λ_{max} = 262 nm (log ϵ = 3.47).

Anal. Calcd for $C_{29}H_{26}O_2$ (406.50): C, 85.68; H, 6.45. Found: C, 85.68; H, 6.31.

3,3-Bis(4-methylphenyl)-*trans*-4,5-diphenyl-1,2-dioxolane (*trans*-4c). ^{1}H NMR: δ 2.13 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 4.71 (d, 1 H, J = 10 Hz), 5.48 (d, 1 H, J = 10 Hz), 6.71–7.52 (m, 18 H, Ar).

The original product mixture, from which the ^{1}H NMR signals of *trans*-**4c** were extracted, showed CH_3 singlets at δ 2.10, 2.13, 2.31, and 2.34 in a ratio of 7:3:7:3, indicating a *cis*-**4c**:*trans*-**4c** ratio of 7:3.

3-(4-Methoxyphenyl)-3,4,5-triphenyl-1,2-dioxolanes (4d). 1-(4-Methoxyphenyl)-1,*trans*-2,3-triphenylcyclopropane (**3d**) (1.5 g, 4.0 mmol) were oxygenated to better than 95% within 5 h. The workup procedure yielded 1.05 g of a gel (64% from ethanol), which, according to ^{1}H NMR analysis, contained α-**4d** and β-**4d** in a ratio of about 3:2.

[(3*S*,4*S*,5*S*)/(3*R*,4*R*,5*R*)]-3-(4-Methoxyphenyl)-3,4,5-triphenyl-1,2-dioxolane (α-4d): ^{1}H NMR: δ 3.77 (s, 3 H, OCH_3), 4.73 (d, 1 H, J = 6 Hz), 5.62 (d, 1 H, J = 6 Hz), 6.94 (m, 19 H, Ar).

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[(3*R*,4*S*,5*S*)/(3*S*,4*R*,5*R*)]-3-(4-Methoxyphenyl)-3,4,5-triphenyl-1,2-dioxolane (β-4d): ^{1}H NMR: δ 3.57 (s, 3 H, OCH_3), 4.73 (d, 1 H, J = 6 Hz), 5.56 (d, 1 H, J = 6 Hz), 6.94 (m, 19 H, Ar).

^{13}C NMR (of α- and β-**4d**): δ 54.9 (q), 55.3 (q), 68.2 (d), 85.7 (d), 93.5 (s).

The solution contained, besides α- and β-**4d**, two more dioxolanes as was revealed by the ^{1}H NMR spectrum, which showed two further OCH_3 groups with singlets at δ 3.65 and 3.82 in a ratio of 3:2, attributed to **[(3*S*,4*S*,5*R*)/(3*R*,4*R*,5*S*)]-** and **[(3*R*,4*S*,5*R*)/(3*S*,4*R*,5*S*)]-3-(4-methoxyphenyl)-3,4,5-triphenyl-1,2-dioxolane, γ-4d and δ-4d**, respectively. When the oily product, obtained after photooxygenation of **3d** and removal of MeCN, was resolved in $CDCl_3$, the four OCH_3 singlets at δ 3.77, 3.57, 3.65, and 3.82 were found in a ratio of 9:6:3:2 (≡ 45:30:15:10).

3,3-Bis(4-methoxyphenyl)-4,5-diphenyl-1,2-dioxolanes (4e). 1,1-Bis(4-methoxyphenyl)-*trans*-2,3-diphenylcyclopropane (**3e**) (1.0 g, 2.4 mmol) was oxygenated within 1 h to better than 95%. The workup procedure yielded 0.6 g of **3,3-bis(4-methoxyphenyl)-*cis*-4,5-diphenyl-1,2-dioxolane (*cis*-4e)** (57%, colorless needles from ethanol), mp 110–111 °C. ^{1}H NMR: δ 3.57 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 4.69 (d, 1 H, J = 5.5 Hz), 5.59 (s, 1 H, J = 5.5 Hz), 6.42–7.68 (m, 18 H, Ar). ^{13}C NMR: δ 54.9 (q), 55.3 (q), 68.3 (d), 85.7 (d), 93.4 (s). UV (CH_2Cl_2): λ_{max} = 265 nm (log ε = 3.63) and 275 nm (log ε = 3.57); shoulder at λ = 285 nm (log ε = 3.40).

Anal. Calcd for $C_{29}H_{26}O_4$ (438.50): C, 79.43; H, 5.98. Found: C, 79.60; H, 5.75.

3,3-Bis(4-methoxyphenyl)-*trans*-4,5-diphenyl-1,2-dioxolane (*trans*-4e). ^{1}H NMR: δ 3.65 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3), 4.68 (d, 1 H, J = 9 Hz), 5.48 (d, 1 H, J = 9 Hz), 6.42–7.68 (m, 18 H, Ar).

The ^{1}H NMR spectrum of the original product mixture, from which the ^{1}H NMR signals of *trans*-**4e** were extracted, showed OCH_3 singlets at 3.57, 3.65, 3.73, and 3.75 in a ratio of 3:2:2:3, indicating a *cis*-**4e**:*trans*-**4e** ratio of 3:2.

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Supplementary Material Available: ^{1}H NMR spectrum of **2c**, ^{13}C NMR spectrum of α-**4b** (or β-**4b**), ^{13}C NMR spectra (off-resonance and noise decoupled) of mixture of (α-**4d** + β-**4d**), ^{1}H NMR spectrum of the original mixture of (α-**4d** + β-**4d** + γ-**4d** + δ-**4d**) used to determine their ratio from the 4 OCH_3 groups at about 4 ppm, and ORTEP drawing of **3e** (7 pages). Ordering information is given on any current masthead page.

Stereoselective Additions of Nucleophilic Alkenes to Chiral Thionium Ions[1]

Ichiro Mori, Paul A. Bartlett, and Clayton H. Heathcock*

Department of Chemistry, University of California, Berkeley, California 94720

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A convenient one-pot process has been developed for conversion of an aldehyde to an arylthionium ion (e.g., Schemes IV and V), which can be trapped by a nucleophilic alkene. The stereochemistry of the reactions of such chiral and prochiral arylthionium ions with achiral and prochiral nucleophilic alkenes has been studied. The major adducts are those predicted by qualitative application of the Cram–Felkin rule. Quantitatively, however, the nature of the thionium aryl group has a marked effect. For example, whereas **12** reacts with the phenylthionium ion derived from 2-phenylpropanol to give keto sulfides **13a** and **14a** in a ratio of 4:1, the corresponding reaction of the mesitylthionium ion affords the analogous keto sulfides **24a** and **25a** in a ratio of >98:2. In reactions between prochiral thionium ions and prochiral enol silanes, good simple (anti) relative stereochemistry is observed, especially with enol silane **35** (Scheme VII, Table IV). Mesitylthionium ions of α-chiral aldehydes react with prochiral enol silanes to give one of the four possible products in predominance (Scheme VIII, Table V). Again, however, enol silane **35** is found to be a superior reagent, giving **41** in 97% stereoisomeric purity. The α-methyl-β-arylthio ketones produced in these thionium ion reactions can be transformed by a straightforward process, which includes desulfurization, into chain compounds having anti 1,3-dimethyl branches (e.g., Scheme IX). An iterative application of this scheme can be used to prepare deoxypolypropionate structures, as shown in Scheme X.

Introduction

In previous papers in this series, we have reported that the diastereofacial preference of a chiral aldehyde derivative is often dependent on the size of the activating ligand X attached to the carbonyl oxygen (eq 1).[1,2] In this paper, we report an extension of this investigation to the related thionium ion system (eq 2).[3] In addition, we have studied the stereoselectivity of reactions of prochiral enol silanes with prochiral and chiral thionium ions (eqs 3 and 4) and have found that excellent stereoselectivity can be observed, even in cases such as that illustrated in eq 4, where four possible diastereomers can be formed. Finally, we demonstrate an application of the thionium ion method for preparation of acyclic systems having 1,3-stereorelationships.

Generation of Thionium Ions. The Pummerer reaction was discovered in 1909 when it was found that treatment of (phenylsulfinyl)acetic acid with acetic anhydride gives α-acetoxy-α-(phenylthio)acetic acid.[4] The reaction has been the subject of mechanistic investigation

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