Salt Effect on the 9,10-Dicyanoanthracene-Sensitized Photooxygenation of 1,2-Diarylcyclopropanes and the Photodecomposition of 3,5-Diaryl-1,2-dioxolanes

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The 9,10-dicyanoanthracene (DCA)-sensitized photooxygenation of less electron-rich 1,2-diarylcyclopropanes **1** such as 1,2-diphenylcyclopropanes and 1,2-bis(4-chlorophenyl)cyclopropanes in the presence of $Mg(ClO_4)_2$ gave *cis*- and *trans*-3,5-diaryl-1,2-dioxolanes as major products. However, in the absence of $Mg(ClO_4)_2$, the photooxygenation did not afford 1,2-dioxolanes, but their decomposition products, 1,3-diaryl-1-hydroxypropan-3-ones **5**, aryl aldehydes **6**, and aryl methyl ketones **7**. The DCA-sensitized photodecomposition of 1,2-dioxolanes also gave **5–7**. This photoreaction was suppressed by the addition of $Mg(ClO_4)_2$. The DCA-sensitized photooxygenation of **1** proceeds via radical cations that are generated by photoinduced electron-transfer from **1** to the excited singlet ^{1}DCA*. The DCA-sensitized photodecomposition of 1,2-dioxolanes occurs via exciplexes that are formed between 1,2-dioxolanes and ^{1}DCA* or energy-transfer from the excited triplet ^{3}DCA* to 1,2-dioxolanes.

Photooxygenation of small-ring compounds via photoinduced electron transfer has received considerable attention in recent years.[1,2] Previously, we reported that the 9,10-dicyanoanthracene (DCA)-sensitized photooxygenation of electron-rich 1,2-diarylcyclopropanes gives 3,5-diaryl-1,2-dioxolanes in high yields.[1a-c] However, the photooxygenation of less electron-rich 1,2-diarylcyclopropanes such as 1,2-diphenylcyclopropane proceeded inefficiently under similar conditions and did not afford 1,2-dioxolanes as isolable products. We now report the photooxygenation of such less electron-rich 1,2-diarylcyclopropanes in the presence of a metal salt[1b,c,2d,3,4b,c] and an aromatic hydrocarbon (cosensitizer).[1b,2a,c,d,4a,c] Since this method made it possible to isolate 1,2-dioxolanes in pure forms, we have also studied their photodecomposition.

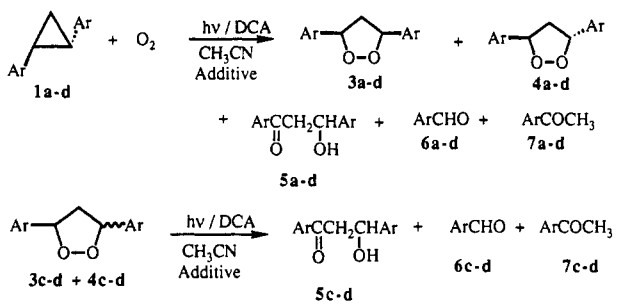
Results and Discussion

Photooxygenation of 1,2-Diarylcyclopropanes. Effect of $Mg(ClO_4)_2$. Acetonitrile solutions containing *trans*-1,2-diarylcyclopropanes **1a–d** and a catalytic amount of DCA (1/20 equiv) were irradiated with >400 nm of light in a stream of oxygen in the absence and presence of $Mg(ClO_4)_2$. The progress of the photooxygenation was followed by GLC and TLC analyses of the reaction mixtures. After complete consumption of the substrates, the products were analyzed by ^{1}H NMR.

The photooxygenation of **1a–c** in the presence of $Mg(ClO_4)_2$ gave *cis*- and *trans*-3,5-diaryl-1,2-dioxolanes **3a–c** and **4a–c** along with aryl aldehydes **6a–c** and aryl methyl ketones **7a–c**. Among these 1,2-dioxolanes, formation of the cis isomers **3a–c** always predominated: **3a**/**4a** = 63/37, **3b**/**4b** = 60/40, and **3c**/**4c** = 73/27. The photooxygenation of *cis*-1,2-diarylcyclopropanes **2a–c** under similar conditions also gave **3a–c** and **4a–c** in the same ratios as those obtained from **1a–c**. The ratios of **3a–c** to **4a–c** remained unchanged throughout the photoreactions and were independent of the concentration of added $Mg(ClO_4)_2$. The DCA-sensitized photooxygenation of **1a–c** in the absence of $Mg(ClO_4)_2$ did not afford the corresponding 1,2-dioxolanes, but gave only the ring-opened oxidation products, 1,3-diaryl-1-hydroxypropan-3-ones **5a–c**,[5] **6a–c**, and **7a–c**.

Similar photooxygenation of electron-rich *trans*-1,2-bis(4-methoxyphenyl)cyclopropane (**1d**) gave exclusively the 1,2-dioxolanes **3d** and **4d** both in the absence and presence of $Mg(ClO_4)_2$ as reported previously.[1a,b] The results are summarized in Table I.

Scheme I



a: Ar = C_6H_5, b: Ar = 4-$CH_3C_6H_4$, c: Ar = 4-ClC_6H_4, d: Ar = 4-$CH_3OC_6H_4$

Effect of Biphenyl. The DCA-sensitized photooxygenation of **1a–c** was markedly accelerated by the addition of biphenyl (BP).[1b,2a,c,d] The rates of consumption of **1a–c** in the presence of BP were two to five times faster than those in the absence of BP. However, the photooxygenation under these conditions did not afford dioxolanes, but gave only the ring-opened oxidation products **5a–c**, **6a–c**, and **7a–c**. The results are also given in Table I.

DCA-Sensitized Photolysis of 3,5-Diaryl-1,2-dioxolanes. The DCA-sensitized photolysis of a 6:4 mixture of **3c** and **4c** was studied in acetonitrile in the absence and presence of BP and $Mg(ClO_4)_2$ under argon atmosphere.

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Table I. DCA-Sensitized Photooxygenation of 1,2-Diarylcyclopropanes[a]

compd	additive	(mol/L)	irradn time (min)	product ratio[b] (%) 3 + 4[c]	5	6	7
1a	none		410	0	40	40	20
	BP	(1.25×10^{-2})	150	0	45	36	19
	$Mg(ClO_4)_2$	(1.25×10^{-2})	305	40	0	40	20
		(2.5×10^{-2})	295	50	0	33	17
		(5.0×10^{-2})	220	42	0	42	16
		(1.0×10^{-1})	120	56	0	25	19
1b	none		410	0	56	28	16
	BP	(1.25×10^{-2})	40	0	70	23	7
	$Mg(ClO_4)_2$	(1.25×10^{-2})	80	44	0	44	12
1c	none		410	0	43	43	14
	BP	(1.25×10^{-2})	30	0	44	44	12
	$Mg(ClO_4)_2$	(1.25×10^{-2})	80	50	0	33	17
1d	none		100	100	0	0	0
	BP	(1.25×10^{-2})	30	100	0	0	0
	$Mg(ClO_4)_2$	(1.25×10^{-2})	30	100	0	0	0

[a] [1] = 2.5×10^{-2} mol/L. [DCA] = 5×10^{-4} mol/L. Conversion ≥95%. [b] Determined by ^1H NMR analyses of the reaction mixtures. [c] **3a/4a** = 63/37. **3b/4b** = 60/40. **3c/4c** = 73/27. **3d/4d** = 70/30.

Table II. DCA-Sensitized Photolysis of 1,2-Dioxolanes in the Absence and Presence of Additives under Argon Atmosphere[a]

compd[b]	solvent	additive	irradn time (min)	conv[c] (%)	product ratio[c] (%) 5	6	7
3c–4c	CH_3CN	none	40	100	80	10	10
3c–4c	CH_3CN	BP	40	91	64	19	17
3c–4c	CH_3CN	$Mg(ClO_4)_2$	40	52	50	27	23
3d–4d	CH_3CN	none	60	18	38	41	21
3d–4d	CH_3CN	none	120	58	55	29	16
3d–4d	CH_3CN	$Mg(ClO_4)_2$	120	35	8	44	48
3d–4d	C_6H_6	none	120	60	9	52	39
3d–4d[d]	CH_3CN	none	120	100	0	0	0

[a] [1,2-Dioxolane] = [BP] = $[Mg(ClO_4)_2] = 1 \times 10^{-2}$ mol/L. [DCA] = 5×10^{-4} mol/L. [b] Cis–trans mixtures (**3c/4c** = 6/4, **3d/4d** = 7/3) were used. [c] Determined by ^1H NMR analyses of the reaction mixtures. [d] Under O_2 atmosphere.

The photolysis without adding any additives gave **5c** as a major product along with small amounts of **6c** and **7c**. The photodecomposition was slightly retarded by the addition of BP, accompanied by a slight increase in the proportion of **6c** and **7c**. The photodecomposition was retarded more effectively by the addition of $Mg(ClO_4)_2$. However, the photodecomposition of a 7:3 mixture of **3d** and **4d** proceeded inefficiently compared to that of **3c** and **4c** under the same reaction conditions. The efficiencies of the photodecomposition were similar both in acetonitrile and in benzene. The results are summarized in Table II.

The DCA-sensitized photolysis of 1,2-dioxolanes in acetonitrile under O_2 gave complex mixtures. However, when the DCA-sensitized photoreaction of a mixture of **3c** and **4c** was carried out in acetonitrile under O_2 in the presence of 3 equiv of 1,2-bis(1-naphthyl)cyclopropane (NCP) under similar conditions, **5c**, **6c**, and **7c** were obtained in a 37:29:34 ratio along with oxidized products of NCP at an early stage (26% conversion of **3c** and **4c**) of the photoreaction: in this photoreaction, NCP was chosen as a cyclopropane substrate for the ease of ^1H NMR analysis of the reaction mixture. These results indicate that 1,2-dioxolanes can be converted into **5–7** by the DCA-sensitized photolysis under O_2, only when a cyclopropane substrate is present in the reaction mixture.

Thermolysis of a 6:4 mixture of **3c** and **4c** at 80 °C for 8 h gave **6c** and **7c** in a quantitative yield,[6] but **3c** and **4c** were stable at 50 °C for 2 h.

Mechanism for Formation of 1,2-Dioxolanes. The fluorescence of DCA in acetonitrile was quenched by **1a–d** at nearly diffusion-controlled rates, but not by $Mg(ClO_4)_2$.

Table III. Rate Constants for the Fluorescence Quenching of DCA, Oxidation Potentials of Cyclopropanes and Other Compounds, and Calculated ΔG Values for the One-Electron Transfer Process from Compounds to $^1DCA^*$ in Acetonitrile

compd	k_q[a] (L mol^{-1} s^{-1})	$E^{ox}_{1/2}$[b] (V)	ΔG[c] (kJ mol^{-1})
1a	1.41×10^{10}	1.07	−52.6
1b	1.55×10^{10}	0.90	−69.5
1c	1.43×10^{10}	1.06	−54.0
1d	1.83×10^{10}	0.55	−103.2
3a–4a[d]		1.88	25.1
3b–4b[d]		1.60	−1.9
3c–4c[d]	1.56×10^{9}	1.75	12.5
3d	1.43×10^{10}	1.27	−33.8
3d	1.36×10^{9}[e]		
BP	4.6×10^{9}	1.45	−16.4

[a] Rate constants for the fluorescence quenching of DCA in aerated CH_3CN: [DCA] = 1×10^{-4} mol/L; τ(DCA, air) = τ(DCA, N_2) × I(DCA, air)/I(DCA, N_2) = 12.8 ns; τ(DCA, N_2) = 15.3 ns; see ref 19. [b] Oxidation potentials (V vs $Ag/AgClO_4$) were determined as half-peak potentials in cyclic voltammetry: Pt electrode, tetraethylammonium perchlorate (0.1 mol/L) in CH_3CN. [c] Calculated value in CH_3CN; see ref. 7. Reduction potential of DCA; −1.33 V. [d] Measured for cis–trans mixtures (**3/4** = 7/3–6/4). [e] In benzene.

The free energy changes (ΔG) estimated by the Rehm–Weller equation[7] for a single-electron transfer from **1a–d** to $^1DCA^*$ were negative. The relevant data are given in Table III. These results strongly suggest that the photooxygenation of the cyclopropane derivatives CP proceeds via cyclopropane radical cation $CP^{\bullet+}$ generated by a single-electron transfer from CP to $^1DCA^*$.

A plausible mechanism for the formation of 1,2-dioxolanes is shown in Scheme II. In this photoreaction, $Mg(ClO_4)_2$ suppresses a back-electron transfer within

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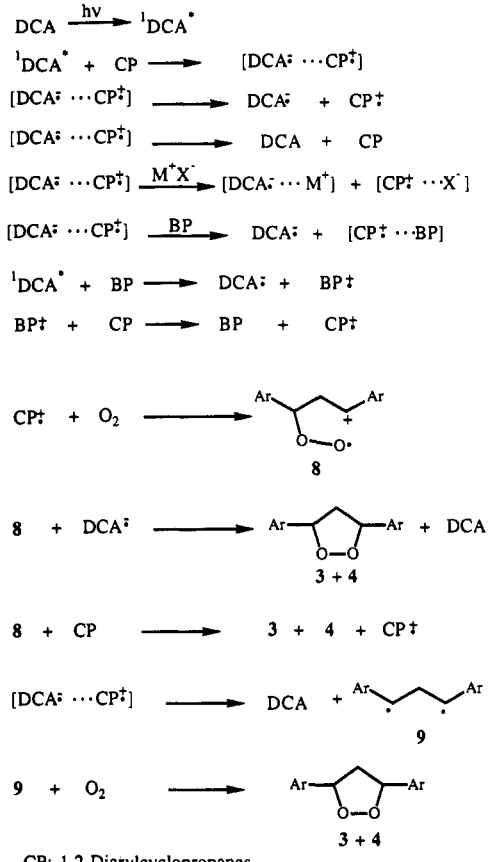
Scheme II



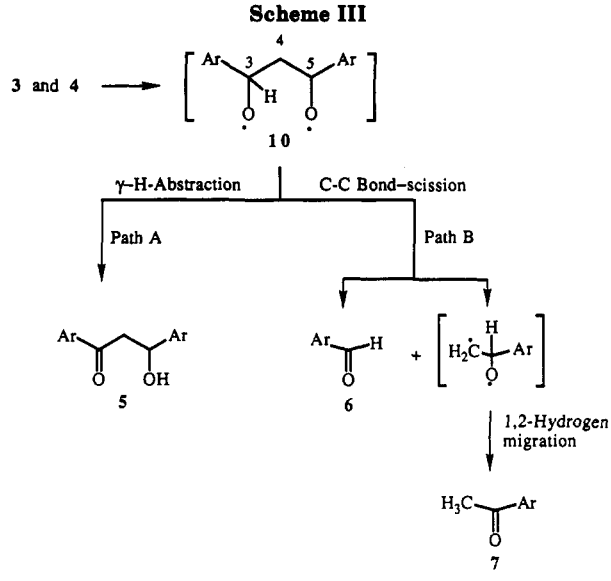
CP: 1,2-Diarylcyclopropanes
M^+X^-: Metal salt
BP: Biphenyl

radical ion pair [$DCA^{\bullet-}$···$CP^{\bullet+}$] and thereby facilitates dissociation of the radical ion pair to solvent-separated radical ions.[1b,c,2d,3,4b,c,8] BP also facilitates the formation of the solvent-separated radical cation $CP^{\bullet+}$.[1b,2a,c,d,4a,c] There are two possibilities for the role of BP. The first possibility is a rapid secondary electron transfer from CP to radical cation $BP^{\bullet+}$, which is generated by a primary electron-transfer from BP to $^1DCA^*$, to form $CP^{\bullet+}$.[9b] The other possibility is the suppression of a back-electron transfer from $DCA^{\bullet-}$ to $CP^{\bullet+}$ via a long-lived π-complex [$CP^{\bullet+}$···BP].[9a] The attack of molecular dioxygen on $CP^{\bullet+}$ gives 1,5-radical cation **8** from which 1,2-dioxolanes are produced. The other possible mode of oxygenation is the attack of molecular dioxygen on a 1,3-biradical **9** which is formed by a back-electron transfer from $DCA^{\bullet-}$ to $CP^{\bullet+}$.[10] That **3a–c** and **4a–c** are formed in the same ratios from both **1a–c** and **2a–c** supports the intermediacy of **8** or **9**.

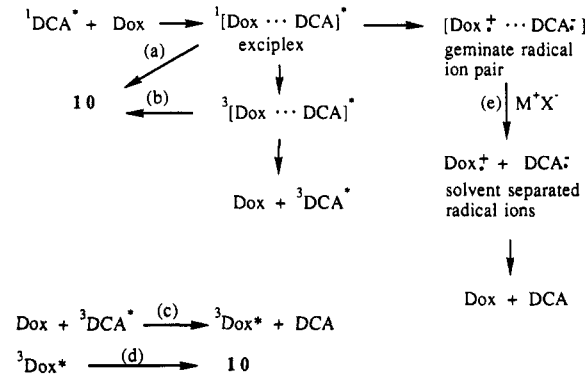
An important observation in this photooxygenation is the effect of $Mg(ClO_4)_2$ on the 1,2-dioxolane-forming reaction: 1,2-Dioxolanes are formed from the less electron-rich cyclopropanes **1a–c** only when $Mg(ClO_4)_2$ is present.

Mechanism for Photodecomposition of 1,2-Dioxolanes. The photooxygenation of **1a–c** in the absence of $Mg(ClO_4)_2$ gave only the ring-opened oxidation products

Scheme III



Scheme IV



Dox: 3,5-Diaryl-1,2-dioxolane
M^+X^-: Metal salt

5a–c, **6a–c**, and **7a–c**, and 1,2-dioxolanes were not obtained. Formation of these oxidation products can be explained in terms of the photodecomposition of 1,2-dioxolanes **3a–c** and **4a–c**. The possibility of thermal decomposition of the 1,2-dioxolanes during the photoreaction is excluded, since they are thermally stable below 50 °C. This is also supported by the fact that the thermal decomposition of **3c** and **4c** at 80 °C in benzene gives **6c** and **7c** without formation of **5c**.[6]

The proposed pathways for the photodecomposition of **3a–c** and **4a–c** are shown in Schemes III and IV. A key intermediate in this reaction is 1,5-dioxy radical **10** which is generated by the cleavage of the O–O bond of **3** and **4**. A γ-hydrogen abstraction by the oxy radical at C_5 gives keto alcohol **5** (path A). On the other hand, C_3–C_4 bond scission in **10**, followed by a 1,2-hydrogen migration, gives aldehyde **6** and ketone **7** (path B). Both pathways occur competitively.

We now discuss the mechanism for the generation of **10**. Several mechanisms could be considered. A plausible mechanism is the O–O bond cleavage of 1,2-dioxolanes (Dox) through exciplex [Dox···DCA]* which is formed by interaction between 1,2-dioxolane and $^1DCA^*$ (paths a and b).[11] Formation of the exciplex is suggested by the fact that the fluorescence of $^1DCA^*$ is quenched efficiently by dioxolanes **3c**, **4c**, and **3d** both in acetonitrile and in benzene. In this case, the exciplex can be either singlet

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^{1}[Dox···DCA]* or triplet ^{3}[Dox···DCA]*.

The other possibility is the pathway involving electronic energy transfer from ^{3}DCA*.[12] If the energy transfer occurs efficiently from ^{3}DCA* (E_T = 160 kJ mol^{-1})[13a] to the dioxolanes via an electron-exchange mechanism (path c), then this process would lead to the O–O bond cleavage of dioxolanes: Note that this process is energetically accessible because the O–O bond energy has been estimated to be around 140 kJ mol^{-1} [14] which is smaller than the E_T energy of ^{3}DCA*. A similar mechanism has been proposed for a photosensitized decomposition of organic peroxides.[15]

It is known that ^{3}DCA* can be quenched by interaction with molecular dioxygen.[12] Therefore, ^{3}DCA* would be quenched by both 1,2-dioxolanes and molecular dioxygen. However, the possibility of path c cannot be ruled out from the following experiments: The photodecomposition of **3d** and **4d** in benzene was sensitized by triplet sensitizers such as benzophenone (E_T = 287 kJ mol^{-1})[16] and fluorenone (E_T = 214 kJ mol^{-1})[15b] (see Experimental Section). This result indicates that the triplet photosensitized reaction also leads to O–O bond cleavage of 1,2-dioxolanes.

Involvement of ^{3}DCA* has been proposed in a variety of DCA-sensitized photoreactions. In our case, ^{3}DCA* could be formed through the quenching of ^{1}DCA* by molecular oxygen[12] or intersystem crossing of the exciplex ^{1}[Dox···DCA]*.[13] The formation of ^{3}DCA* through direct intersystem crossing of ^{1}DCA* appears not to be a major pathway, because the quantum yield for this process is known to be very small (ϕ(^{1}DCA* → ^{3}DCA*) = 0.03).[12b]

It should also be mentioned that the electron transfer from 1,2-dioxolanes to ^{1}DCA* is not involved as a major pathway for the photodecomposition of 1,2-dioxolanes, because this process is endothermic except for **3d** and **4d** (Table III). Note also that although electron transfer from **3d** and **4d** to ^{1}DCA* is highly exothermic, the DCA-sensitized photodecomposition of these compounds in acetonitrile was much slower than those of **3c** and **4c** and proceeded at similar rates both in acetonitrile and in benzene (Table II). Furthermore, the rate for the DCA-sensitized photodecomposition of **3c** and **4c** was appreciably decreased by the addition of $Mg(ClO_4)_2$, which promotes the formation of solvent-separated radical ions (path e). All these results suggest that the radical cations of 1,2-dioxolanes are stable species and do not undergo the O–O bond cleavage.

Noteworthy is that, in the photooxygenation of **1a–c** and the photodecomposition of **3c–d** and **4c–d**, formation of keto alcohols **5a–d** was depressed by adding $Mg(ClO_4)_2$. This suggests that the photodecomposition of **5a–d** is accelerated by $Mg(ClO_4)_2$, and this suggestion was partly evidenced by the following experiments: Keto alcohol **5a** rapidly decomposed to give benzoic acid upon irradiation in acetonitrile under O_2 in the presence of $Mg(ClO_4)_2$, whereas the photoreaction of **5a** under similar conditions in the absence of $Mg(ClO_4)_2$ gave a complex mixture which contains only small amount of benzoic acid and a large quantity of polymeric materials. Furthermore, the rate of decomposition of **5a** in the presence of $Mg(ClO_4)_2$ was more than two times faster, compared to that in the absence of $Mg(ClO_4)_2$. These results indicate that the decomposition of **5** is accelerated by $Mg(ClO_4)_2$, probably through a chelation of Mg^{2+} ion with the carbonyl oxygen of **5**.

Experimental Section[17]

Materials. All the cyclopropane derivatives were synthesized and purified by the methods described previously.[1b] 1,3-Diphenyl-1-hydroxypropane-3-one[5] (**5a**) was synthesized according to the method of literature.[18] Other organic chemicals were purchased and purified by distillation or recrystallization. $Mg(ClO_4)_2$ was also purchased (Kishida) and used without further purification.

General Procedure for DCA-Sensitized Photooxygenation of 1,2-Diarylcyclopropanes. A solution of a cyclopropane derivative (0.2 mmol) and DCA (0.01 mmol) in dry acetonitrile (8 mL) in the absence or presence of additive was irradiated at room temperature with a 500-W high-pressure Hg arc through an aqueous NH_3–$CuSO_4$ filter solution in a stream of O_2. The progress of the reaction was followed by GLC analysis of the reaction mixture. After the consumption of the cyclopropane, the solvent was removed under reduced pressure. The residue was extracted with hexane. The extract was washed with water, dried (Na_2SO_4), and evaporated. The residue was analyzed from its 60- or 270-MHz ^{1}H NMR spectral data, and the product ratio was determined by integration of the signals. The results are summarized in Table I.

DCA-Sensitized Photooxygenation of 1c for Preparative Runs. A mixture of **1c** (5 mmol), $Mg(ClO_4)_2$ (5 mmol), and DCA (0.015 mmol) in anhydrous acetonitrile (75 mL) was irradiated for 3 h with O_2 bubbling through, and the solvent was removed. The residue was extracted with hexane. The solvent, **6c**, and **7c** were evaporated under reduced pressure giving a crude mixture of **3c** and **4c** (634 mg, 43%). Recrystallization of the residue from hexane gave a mixture of **3c** and **4c** (177 mg, 12%) in almost pure state. Mixtures of **3a–b** and **4a–b** were obtained in a similar manner. Dioxolanes **3a–c** and **4a–c** were unstable toward chromatography on silica gel and alumina and could not be separated by recrystallization. The structure and the product ratios were determined by ^{1}H NMR spectra of mixtures of **3a–c** and **4a–c** compared with those of **3d** and **4d** which could be separated and isolated in pure forms by recrystallization from hexane.[1b]

Physical Properties of 1,2-Dioxolanes.

cis-3,5-Diphenyl-1,2-dioxolane (**3a**): ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.72 (dt, 1 H, J = 8 and 12 Hz), 3.58 (dt, 1 H), 5.45 (t, 2 H, J = 8 Hz), 7.26 (s, 10 H); ^{13}C NMR δ 51.7, 83.4, 126.7, 128.3, 128.7, 138.7.

trans-3,5-Diphenyl-1,2-dioxolane (**4a**): ^{1}H NMR (60 MHz, $CDCl_3$) δ 3.06 (t, 2 H, J = 7 Hz), 5.47 (t, 2 H), 7.3 (s, 10 H); ^{13}C NMR δ 51.1, 82.8, 126.6, 128.4, 128.7, 138.5. **4a** including a small amount of **3a**: IR (KBr) 1690, 1600, 1460, 1370, 1270, 1210, 760 cm^{-1}. MS (20 eV) m/z 226 (M^+). Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.67; H, 6.34.

cis-3,5-Bis(4-methylphenyl)-1,2-dioxolane (**3b**): ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.35 (s, 6 H), 2.68 (dt, 1 H, J = 8 and 12 Hz), 3.40 (dt, 1 H), 5.40 (t, 2 H, J = 8 Hz), 7.15 (s, 8 H); ^{13}C NMR δ 21.2, 51.5, 83.3, 126.6, 129.3, 135.6, 138.1. **3b** including small amounts of **4b**: IR (KBr) 1680, 1620, 1520, 1430, 1310, 1190, 1120, 1030, 920, 820 cm^{-1}; MS (20 eV) m/z 254 (M^+). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.27; H, 7.16.

trans-3,5-Bis(4-methylphenyl)-1,2-dioxolane (**4b**): ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.36 (s, 6 H), 3.00 (t, 2 H, J = 7 Hz), 5.44 (t, 2 H), 7.18 (s, 8 H); ^{13}C NMR δ 21.7, 50.8, 82.9, 126.8, 129.2, 135.2, 138.3.

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cis-3,5-Bis(4-chlorophenyl)-1,2-dioxolane (**3c**): ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.60 (dt, 1 H, J = 7 and 12 Hz), 3.47 (dt, 1 H), 5.41 (t, 2 H, J = 7 Hz), 7.16 (s, 8 H); ^{13}C NMR δ 51.5, 82.6, 127.9, 129.0, 134.2, 137.2. **3c** including small amounts of **4c**: IR (KBr) 1690, 1600, 1500, 1100, 1020, 840 cm^{-1}; MS (20 eV) m/z 298, 300 (M^+). Anal. Calcd for $C_{15}H_{12}O_2Cl_2$: C, 61.03; H, 4.09. Found: C, 60.97; H, 4.18.

trans-3,5-Bis(4-chlorophenyl)-1,2-dioxolane (**4c**): ^{1}H NMR (60 MHz, $CDCl_3$) δ 3.00 (t, 2 H, J = 7 Hz), 5.41 (t, 2 H), 7.27 (s, 8 H); ^{13}C NMR δ 51.1, 81.9, 127.9, 129.0, 134.3, 137.2.

Typical Procedure for DCA-Sensitized Photolysis of 1,2-Dioxolane. An acetonitrile solution (4 mL) containing a 6:4 mixture of **3c** and **4c** (4×10^{-2} mmol) and DCA (2.2×10^{-3} mmol) in the presence of biphenyl or $Mg(ClO_4)_2$ (4×10^{-2} mmol) were irradiated under argon or O_2 atmosphere through an aqueous NH_3–$CuSO_4$ filter solution using a merry-go-round apparatus for 40 min. The reaction mixture was analyzed by ^{1}H NMR. The product ratio was determined by integration of the signals. The results are shown in Table II.

DCA-Sensitized Photolysis of 3d and 4d for Preparative Runs. A 7:3 mixture of **3d** and **4d** (0.2 mmol) and DCA (0.01 mmol) in acetonitrile (8 mL) was irradiated for 3 h under argon atmosphere, and the solvent was removed. ^{1}H NMR analysis of the reaction mixture showed the formation of **5d**, **6d**, and **7d** in a 57:29:14 ratio. Formation of **6d** and **7d** was confirmed by the comparison of the spectra with an authentic sample. The reaction mixture was chromatographed on silica gel. Elution with EtOAc–benzene (2:8) gave 1,3-bis(4-methoxyphenyl)-1-hydroxypropan-3-one (**5d**, 23 mg, 40%): ^{1}H NMR (60 MHz, $CDCl_3$) δ 3.23 (d, 2 H, J = 6 Hz), 3.72 (s, 3 H), 3.77 (s, 3 H), 5.18 (t, 1 H, J = 6 Hz), 7.00 (ABq, 4 H, $\Delta\nu$ = 26 Hz, J = 8 Hz), 7.29 (ABq, 4 H, $\Delta\nu$ = 60 Hz, J = 8 Hz); ^{13}C NMR δ 46.8, 69.8, 55.5, 55.3, 113.8, 113.9, 127.0, 129.7, 130.5, 135.3, 159.1, 163.9, 198.8; IR (neat) 1660, 1600, 1510, 1250, 1170, 1030, 830 cm^{-1}; MS (70 eV) m/z 268 (M^+).

Thermolysis of 1,2-Dioxolane. A solution of a 6:4 mixture of **3c** and **4c** (4×10^{-2} mmol) in benzene was refluxed for 8 h under N_2. ^{1}H NMR analysis of the reaction mixture showed the formation of **6d** and **7d** in a 1:1 ratio.[6] Similar solution in acetonitrile was stirred for 2 h at 50 °C, and the 1,2-dioxolanes were recovered quantitatively.

Triplet-Sensitized Photolysis of 1,2-Dioxolanes. A benzene solution (4 mL) containing a 6:4 mixture of **3d** and **4d** (4×10^{-2} mmol) in the presence of benzophenone (0.1 mmol) was irradiated under argon atmosphere through a Toshiba UV-35 glass filter (>320 nm) for 100 min. ^{1}H NMR analysis showed the formation of **5d**, **6d**, and **7d** in a 27:52:21 ratio (conv: 69%). Similar irradiation in the presence of fluorenone through an aqueous $NaNO_2$ filter solution (>400 nm) for 35 min gave **5d**, **6d**, and **7d** in a 33:50:17 ratio (conv: 95%). Irradiation without triplet sensitizer under the same conditions gave **3d** and **4d** quantitatively.

DCA-Sensitized Photolysis of a Keto Alcohol. An acetonitrile solution (16 mL) containing **5a** (0.15 mmol) and DCA (0.035 mmol) in the presence of $Mg(ClO_4)_2$ (0.8 mmol) was irradiated with O_2 bubbling for 4 h, and the solvent was removed. The reaction mixture was chromatographed on silica gel to give benzoic acid (12 mg, 66%). An acetonitrile solution (4 mL) containing **5a** (4×10^{-2} mmol) and DCA (2.2×10^{-3} mmol) in the presence of $Mg(ClO_4)_2$ (0.2 mmol) was irradiated under O_2 atmosphere using a merry-go-round apparatus for 180 min. ^{1}H NMR analysis showed the formation of benzoic acid (conv: 74%). In the absence of $Mg(ClO_4)_2$, a complex mixture which contains only small amount of benzoic acid and large quantities of polymeric material was formed (conv: 40%).

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for **3a–4a**, **3b–4b**, **3c–4c**, and **5d** (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Synthesis of Brexan-2-one and Ring-Expanded Congeners

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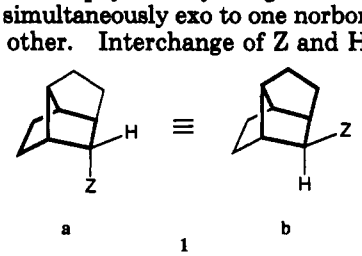
We report an efficient eight-step synthesis (26% overall yield) of brexan-2-one (tricyclo[4.3.0.0^{3,7}]nonan-2-one, **12**). This ketone then served as a convenient precursor to the mechanistically useful molecules, homobrexan-2-one (tricyclo[5.3.0.0^{4,8}]decan-2-one, **14**) and homobrexene (tricyclo[5.3.0.0^{4,8}]dec-2-ene, **20**). Several homologation sequences for the preparation of **14** were developed and can be easily adapted to allow selective introduction of ^{13}C and ^{2}H labels in **14** and **20** for various mechanistic studies.

Introduction

The tricyclic brexane skeleton **1** is comprised of two partially superposed norbornyl units (see bold lines in **1a** and **1b**),[1] and its C_2 symmetry relegates a substituent Z at C-2 to be simultaneously exo to one norbornyl unit and endo to the other. Interchange of Z and H at that site



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produces neither an enantiomer nor a diastereomer but a structure superposable upon the original (i.e., **1a** ≡ **1b**). This unique situation, along with the skeletal rigidity, has led researchers to use brexyl systems for a variety of mechanistic and synthetic studies.

For example, mechanistic studies of brexyl 2-brosylate (**1**, Z = OBs) and related compounds have provided new data[2] relevant to the long-standing, but currently quiescent, debates[3] about solvolysis behavior of *exo*- and

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