the nitrogen hfsc as well if the solvent has a sufficiently low effective dielectric constant.

Experimental Section

Sealed ampules of 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) were obtained from Sigma and used without further purification. The substituted phenyl iodides were obtained from Aldrich (*p*-OCH_3, *m*-CH_3, H, *m*-OCH_3, *p*-Cl, *m*-Cl, *m*-NO_2, *p*-NO_2), ICN (*p*-CH_3), Pierce (*m*-CF_3), or Eastman Kodak (*p*-CN); all of these compounds were used as received. Benzene (Aldrich "gold label") was used without further purification.

A stock solution of DMPO was prepared by dissolving 1.0 g in 100 mL of benzene; this gave a solution having approximately 0.08 M DMPO. Benzene solutions of the substituted phenyl iodides were prepared by dissolving sufficient amounts of each substrate so as to give a concentration of 0.1 M. Reaction mixtures were then prepared by mixing equal volumes of the stock DMPO solution with each of the substituted phenyl iodide solutions. Thus, the final concentrations were 0.04 M DMPO and 0.05 M substituted phenyl iodide. Aliquots (ca. 0.5 mL each) of these reaction mixtures were then transferred to at least six standard ESR tubes, and the solutions were degassed with nitrogen.

The tubes containing the solutions of DMPO and phenyl iodides were then placed in the cavity of the ESR instrument (IBM ER 100D) and continually photolyzed at room temperature with a 200-W Hg source through the radiation grid in the front of the cavity. Typically, three 50-s scans were accumulated for each experiment. Rapid acquisition of the spectra (within 1 min after the start of photolysis) was generally necessary since the molecular iodine resulting from the combination of the iodine atoms formed in eq 1 rapidly quenched the nitroxide spin adducts.

Acknowledgment. I gratefully acknowledge the encouragement and helpful discussions with Professors William A. Pryor and Richard D. Gandour. This work was supported by a grant to W.A.P. by the National Science Foundation (CHE-8303497) and by a contract to W.A.P. from the National Foundation for Cancer Research.

Registry No. DMPO, 3317-61-1; *p*-$MeOC_6H_4I$, 696-62-8; *p*-MeC_6H_4I, 624-31-7; *m*-MeC_6H_4I, 625-95-6; PhI, 591-50-4; *m*-$MeOC_6H_4I$, 766-85-8; *p*-ClC_6H_4I, 637-87-6; *m*-ClC_6H_4I, 625-99-0; *m*-$CF_3C_6H_4I$, 401-81-0; *p*-CNC_6H_4I, 3058-39-7; *m*-$NO_2C_6H_4I$, 645-00-1; *p*-$NO_2C_6H_4I$, 636-98-6; [2,2-dimethyl-5-(*p*-methoxyphenyl)-1-pyrrolidinyl]oxy, 100655-66-1; [2,2-dimethyl-5-(*p*-methylphenyl)-1-pyrrolidinyl]oxy, 100655-67-2; [2,2-dimethyl-5-(*m*-methylphenyl)-1-pyrrolidinyl]oxy, 100655-68-3; (2,2-dimethyl-5-phenyl-1-pyrrolidinyl)oxy, 40936-12-7; [2,2-dimethyl-5-(*m*-methoxyphenyl)-1-pyrrolidinyl]oxy, 100655-69-4; [2,2-dimethyl-5-(*p*-chlorophenyl)-1-pyrrolidinyl]oxy, 100655-70-7; [2,2-dimethyl-5-(*m*-chlorophenyl)-1-pyrrolidinyl]oxy, 100655-71-8; [2,2-dimethyl-5-[*m*-(trifluoromethyl)phenyl]-1-pyrrolidinyl]oxy, 100655-72-9; [2,2-dimethyl-5-(*p*-cyanophenyl)-1-pyrrolidinyl]oxy, 100655-73-0; [2,2-dimethyl-5-(*m*-nitrophenyl)-1-pyrrolidinyl]oxy, 100655-74-1; [2,2-dimethyl-5-(*p*-nitrophenyl)-1-pyrrolidinyl]oxy, 100655-75-2.

Dye-Sensitized Photooxygenation of 1,2-Cyclopentanediones in Methanol

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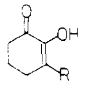
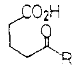
In previous papers,[1] we have reported the dye-sensitized photooxygenation of 1,2-cyclohexanediones (1). The reaction with singlet oxygen has been shown to proceed via an endoperoxide 4, which either liberates carbon monoxide to afford δ-keto acid 2 or is attacked by solvent alcohol to produce α-hydroxyadipic acid monoester 3. Interestingly the product distribution has been found to be highly dependent upon the reaction temperature. The intermediacy of endoperoxide 4 has been discussed on the basis of products 2 and 3, as well as CO and CO_2 liberated.



1



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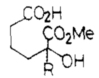

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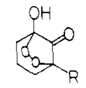

4

On the other hand, 3-methyl-1,2-cyclopentanedione (**5a**) was reported by Wasserman and Pickett[2] to undergo dye-sensitized photooxygenation in the presence of fluoride in chloroform to give 4-oxopentanoic acid (**6a**) with liberation of carbon monoxide. It was considered worthwhile to examine how 1,2-cyclopentanediones (**5**) react with singlet oxygen in alcohol and compare the result with that of **1** to obtain any information about the dye-sensitized photooxygenation.

Results and Discussion

The results of the reaction are listed in Table I. The reaction provides two kinds of products: γ-keto acid **6** with liberation of carbon monoxide and methyl α-hydroxyglutarate **7** presumably formed by trapping the intermediate **8** by methanol. Thus, the reaction path shown in Scheme I can be formulated in the same way as that for 1,2-cyclohexanediones (**1**).[1] The path through the five-membered endoperoxide **8** should be major and the one through the four-membered dioxetane **9** should be minor, as judged from the amount of CO_2 liberated[3] and the yields of **6** and **7** produced. Although the situation seems to be the same, there is a marked difference in the product distribution between **5** and **1**. For the diones **5a** and **5b**, methyl α-hydroxyglutarate **7a** and **7b** were the major products, γ-keto acids **6a** and **6b** being the minor ones or obtained only in trace amounts, whereas, for the diones **1**, δ-keto acids **2** were the major products, methyl α-hydroxyadipates **3** being the minor ones. The very low amounts of CO and CO_2 as shown in Table I also indicate that the major decomposition path of **8** is the trapping by solvent leading to **7**. A rationale to explain the predominance of **7** is as follows. The endoperoxide **8** derived from **5** reacts much more readily with methanol than the endoperoxide **4** derived from **1**, probably owing to the ease with which methanol molecules can approach the carbonyl carbon (Figure 1).

The temperature dependency of the product distribution is observed only for **5a** (Table I), to a lesser extent than that for **1b**.[1] This can be a consequence of the enhanced reactivity of **8**, leading to **7** as discussed above.

An interesting but inexplicable fact is the decreased reactivity of the dione **5** toward singlet oxygen as compared with the dione **1**. From the reaction time and the amount of the dione recovered, it can be concluded that the dione **5** reacts with singlet oxygen several times as slow as the dione **1**. A direct competition of **5a** and **1a** toward singlet oxygen indicated that **5a** reacts with singlet oxygen 5.5

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[1] Utaka, M.; Nakatani, M.; Takeda, A. *Tetrahedron Lett.* **1983**, *24*, 803; *Tetrahedron* **1985**, *41*, 2163.

[2] Wasserman, H. H.; Pickett, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 4695; *Tetrahedron* **1985**, *41*, 2155.

[3] The photosensitized decarboxylation of α-keto acid has been reported. See: Davidson, R. S. *Tetrahedron Lett.* **1976**, 4181. Jefford, C. W.; Exarchou, A.; Cadby, P. A. *Ibid.* **1978**, 2053. Moriarty, R. M.; Chin, A.; Tucker, M. P. *J. Am. Chem. Soc.* **1978**, *100*, 5578. Sawaki, Y.; Ogata, Y. *Ibid.* **1981**, *103*, 6455.

0022-3263/86/1951-1140$01.50/0

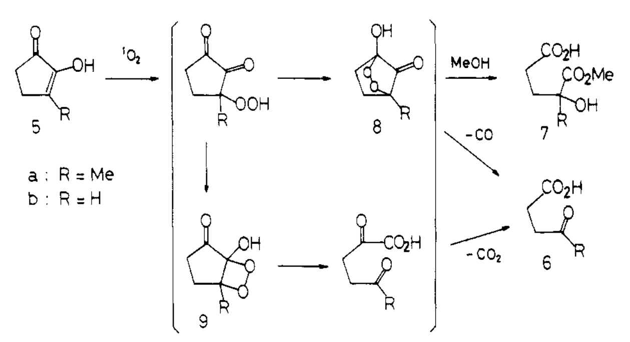
Table I. Dye-Sensitized Photooxygenation of 1,2-Cyclopentanediones (5) in Methanol

				yield, %			gas anal.,[b] %		
substrate	sens[a]	temp, °C	time, h	**6a**	**7a**	**5a**	O_2	CO	CO_2
5a	RB	40	13	20	76[c]	0	134	8	1
		0	15	6	84	0	90	4	0
		-65	17	2	6	84	11	0	0
	MB	40	13	14	61	10	90	7	2
		0	15	10	85	0	98	4	0

				yield, %			gas anal.,[b] %		
substrate	sens[a]	temp, °C	time, h	**6b**	**7b**	**5b**	O_2	CO	CO_2
5b	RB	40	26	trace	56[d]	23	72	1	1
		0	26	trace	39[d]	39	59	1	1
	MB	40	26	trace	35	2	87	2	5

[a] RB = Rose Bengal, MB = methylene blue. [b] Relative to the mole of **5** used. For O_2, percent absorbed; for CO and CO_2, percent evolved. [c] Including the corresponding γ-lactone in 6% yield. [d] Including a trace of corresponding γ-lactone.

Scheme I



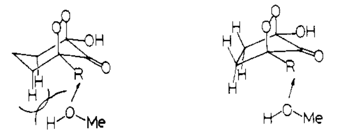


Figure 1.

times as slow as **1a**. Although the dione **5** requires a longer reaction time, the reaction is rather clean, the sum of products **6** and **7** and recovered **5** usually accounting for more than 80% of the initially used **5**.[4]

Experimental Section

General Methods. Distillation of the reaction products or their derivatives were done by using a Kugelrohr oven. GLPC analyses were done by using an SE-30 column. Gas analyses were performed by using a gas chromatograph with molecular sieves for O_2 and CO and with silica gel for O_2 and CO_2.

Materials. Methanol was purified by distillation after treatment with magnesium. Rose Bengal from Chroma-Gesellschaft and methylene blue from Nakarai Chemicals Co. were used as received. 3-Methyl-1,2-cyclopentanedione (**5a**) from Aldrich Chemical Co. was used as received. 1,2-Cyclopentanedione (**5b**) was prepared according to the method reported.[5]

Dye-Sensitized Photooxygenation. The same procedure as described earlier for 1,2-cyclohexanediones (**1**) was adopted.[1] A solution of **5** (2 mmol) and sensitizer (3 mg) in MeOH (10 mL) was irradiated with a 100-W tungsten-halogen lamp (no filter) under an oxygen atmosphere. The solution was stirred magnetically. Absorption of O_2 and liberation of CO were followed by both manometry and GC. After the reaction was completed, the solvent was evaporated and the residual oil was checked by using NMR spectra. Then, the oil was treated with diazomethane in ether and distilled [up to 180 °C (2 mmHg)] to give a colorless oil, which was analyzed by GLC. Analytical samples were obtained by preparative GLC or TLC.

Competition between 5a and 1a toward Singlet Oxygen. Competition was carried out with a solution of **5a** (2 mmol), **1a** (2 mmol), and Rose Bengal (3 mg) in MeOH (20 mL). The solution was irradiated at 30 °C for 3 h under O_2 with stirring. The MeOH was then removed under vacuum, and the residual semisolid was analyzed with ^1H NMR spectra. The material contained **5a**, **7a**, **1a**, and **2a** in a mole ratio of 0.90:0.10:0.45:0.55 as calculated by the integrated intensities of ^1H NMR signals.

4-Oxopentanoic Acid (6a). The acid was converted to its methyl ester with diazomethane and identified by comparing its IR and NMR spectra with those of authentic sample commercially available.

Methyl 4-Carboxy-2-hydroxy-2-methylbutanoate (7a): ^1H NMR ($CDCl_3$) δ 1.42 (s, 3 H), 1.85–2.8 (m, 4 H), 3.4 (br s), 3.77 (s, 3 H), 6.6 (br s).

4-(Methoxycarbonyl)-4-pentanolide. This γ-lactone was obtained by refluxing **7a** in benzene with *p*-TsOH for 1 h: bp 110 °C (3 mmHg); IR (neat) 1785, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.66 (s, 3 H), 1.9–2.8 (m, 4 H), 3.78 (s, 3 H). Anal. Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.37. Found: C, 52.85; H, 6.12.

Methyl 2-Hydroxy-4-(methoxycarbonyl)-2-methylbutanoate: bp 95–105 °C (1 mmHg); IR (neat) 3550, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.41 (s, 4 H), 1.85–2.8 (m, 4 H), 3.4 (br s), 3.65 (s, 3 H), 3.77 (s, 3 H). Anal. Calcd for $C_8H_{14}O_5$: C, 50.52; H, 7.42. Found: C, 50.64; H, 7.41.

4-Oxobutanoic Acid (6b).[6] The presence of a trace of this acid was indicated by the ^1H NMR spectrum, showing a trace of aldehydic proton at δ 9.80.

Methyl 4-Carboxy-2-hydroxybutanoate (7b): ^1H NMR ($CDCl_3$) δ 1.7–2.3 (m, 2 H), 2.35–2.7 (m, 2 H), 3.78 (s, 3 H), 4.28 (dd, *J* = 4.5, 7.0 Hz, 1 H), 6.7 (br s).

4-(Methoxycarbonyl)-4-butanolide. The authentic sample of this lactone was prepared from glutamic acid according to the method reported.[7]

Methyl 2-Hydroxy-4-(methoxycarbonyl)butanoate: bp 105 °C (1.5 mmHg); IR (neat) 3500, 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.7–2.3 (m, 2 H), 2.35–2.7 (m, 2 H), 3.67 (s, 3 H), 3.78 (s, 3 H), 4.22 (dd, *J* = 4.5, 7.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 29.3 (t), 29.5 (t), 51.8 (q), 52.6 (q), 69.6 (d), 173.8 (s), 175.0 (s). These spectral data agreed with those of authentic sample prepared by reduction of dimethyl α-ketoglutarate with $NaBH_4$.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (No. 58550571) from the Ministry of Education, Science and Culture of Japan.

Registry No. **1a**, 3400-78-0; **2a**, 3128-06-1; **5a**, 2758-18-1; **5b**, 10493-98-8; **6a**, 123-76-2; **7a**, 100813-24-9; **7b**, 100813-25-0; MeOH, 67-56-1; $MeOC(O)(CH_2)_2CH(OH)C(O)OMe$, 81077-10-3; $MeOC(O)(CH_2)_2C(OH)(CH_3)C(O)OMe$, 100813-27-2; 4-(methoxycarbonyl)-4-pentanolide, 100813-26-1.

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(4) Only one exception is the reaction carried out by using methylene blue as sensitizer for **5b**, wherein at least nine products were detected by GLPC.

(5) Acheson, R. M. *J. Chem. Soc.* **1956**, 4232.

(6) Shea, K. J.; Wada, E. *J. Am. Chem. Soc.* **1982**, *104*, 5715.

(7) Plieninger, H.; Ege, G.; Fischer, R.; Hoffmann, W. *Chem. Ber.* **1961**, *94*, 2106.