# DYE-SENSITIZED PHOTO-OXYGENATION OF 1,2-CYCLOHEXANEDIONES

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Abstract — The dye-sensitized photo-oxygenation of the enols of 1,2-cyclohexanedione (1) has been carried out in various solvents at  $-70^{\circ}$ -40°. Singlet oxygen is involved in the reaction as evidenced by quenching and rate enhancement observed in deuterated methanol. The reaction proceeds by an ene reaction with singlet oxygen to afford the hydroperoxide, 4, which closes to a five-membered endoperoxide, 5, as a major path or to dioxetane (6) as a minor one. The endoperoxide, 5, decomposed to 5-oxoalkanoic acid (2) with evolution of carbon monoxide or was trapped by the solvent (MeOH or EtOH) to give methyl or ethyl 5-carboxy-2-hydroxypentanoate (3). Competition between the enol of 3-methyl-1,2-cyclohexanedione (1a) and 2,3-dimethyl-2-butene (TME) has shown that the enol is as reactive as TME toward singlet oxygen.

The reactions of electrophilic singlet oxygen with electron-rich systems such as enamines,<sup>1a</sup> enol ethers,<sup>1a,b</sup> enol silyl ethers<sup>1b</sup> and polyalkyl-substituted olefins<sup>1b</sup> have been extensively studied. However, only a few enolic compounds<sup>2</sup> have been subjected to the dye-sensitized photo-oxygenation, until Wasserman and Pickett<sup>3</sup> and the present authors<sup>4</sup> disclosed independently that the enol tautomers of 1,2-cyclohexanediones (1) undergo the dye-sensitized photo-oxygenation to afford keto acids (2) and carbon monoxide. The authors also demonstrated that the photo-oxygenation could be applied successfully to the synthesis of jasmine lactone and related  $\delta$ -lactones.<sup>5</sup>

The enol of 1,2-cyclohexanedione cannot be simply classified as electron-rich because the C—C double bond is conjugated with the electron-withdrawing CO group. In fact, Wasserman needed to use tetrabutylammonium fluoride to promote the reaction since it was sluggish in chloroform with severe dye bleaching. The role of fluoride ion was supposed to be associated with H-bonding phenomena leading to increased electron density on the enol oxygen. In contrast to his results, we have found that the reaction proceeded rather smoothly in MeOH in the absence of promoter without being accompanied by apparent dye bleaching. Interestingly, unsaturated side chains of 1,2-cyclohexanedione remained intact during the photooxygenation.<sup>5</sup> Singlet oxygen is supposed to be involved in the reactions although unambiguous evidence has not been presented. Therefore, it will be desirable to characterize the active species and to clarify the reactivity of 1,2-cyclohexanediones (1) in the dyesensitized photo-oxygenation. This paper deals with these subjects, including full details of our preliminary report.<sup>4</sup>



#### **RESULTS AND DISCUSSION**

Dye-sensitized photo-oxygenation of 3-methyl-1,2cyclohexanedione (1a)

The reaction was carried out in various solvents, such as MeOH, pyridine, acetonitrile and chloroform (Table 1). Judging from the reaction time, product yield and ease of work-up, it is apparent that MeOH or acetonitrile are favourable choices. MeOH is expected to activate the substrate by forming a weak H-bond with the enol hydrogen. However, considering that acetonitrile has a much poorer H-bond acceptor

| Solvent  | Sensitizer* | Temperature<br>(°) | Time | Yield      | d (%) | Gas analysis (%) <sup>b</sup> |            |     |  |
|----------|-------------|--------------------|------|------------|-------|-------------------------------|------------|-----|--|
|          |             |                    | (hr) | 2 <b>a</b> | 3a    | O2                            | cò         | CO3 |  |
| МєОН     | RB          | 40                 | 4    | 91         | 0     | 95                            | 86         | 0   |  |
|          |             | 0                  | 5    | 91         | 2     | 96                            | 87         | 0   |  |
|          |             | -65                | 9    | 91         | 3     | 82                            | 7 <b>7</b> | 0   |  |
|          | MB          | 40                 | 4    | 92         | 2     | 89                            | 84         | 0   |  |
|          |             | 0                  | 5    | 90         | 2     | 99                            | 93         | 0   |  |
|          |             | -65                | 9    | 87         | 5     | 87                            | 81         | 0   |  |
| Pyridine | RB          | 0                  | 5    | 80         |       | 77                            | 81         | 3   |  |
| MeCN     | MB          | Ō                  | 4    | 90         |       | 99                            | 84         | 0.5 |  |
| CHCl     | MB          | Ō                  | 8    | 62         |       | 64                            | 42         | 1   |  |

Table 1. Dye-sensitized photo-oxygenation of 3-methyl-1,2-cyclohexanedione (1a)

\* RB, Rose Bengal; MB, methylene blue

<sup>b</sup>O<sub>2</sub> absorbed, CO and CO<sub>2</sub> evolved.

° 34% of the starting 1a was recovered. Severe dye bleaching was observed.



Scheme 1.

capability than methanol,<sup>6</sup> it can be said that the Hbond formation is not the sole prerequisite for photooxygenation. 5-Oxohexanoic acid (2a) was formed in over 90% yield, which may well correspond to the amounts of oxygen absorbed and carbon monoxide evolved. The formation of methyl 5-carboxy-2hydroxy-2-methylpentanoate (3a) can be taken as a trapping of unstable endoperoxide, 5a, by MeOH (Scheme 1). In order to determine whether or not singlet oxygen is involved in the present reaction, quenching experiments and measurement of the reaction rates in CD<sub>3</sub>OD were carried out, the results being included in Tables 2 and 3, respectively. As is apparent from Table 2. the reaction is effectively retarded by guenchers, such as Dabco, sodium azide and  $\beta$ -carotene. The observed order of effectiveness is as expected from the singlet oxygen-quenching rate constants of these quenchers.<sup>7</sup><sup>+</sup>

In accord with the quenching experiments, a large solvent deuteration effect of  $k(CD_3OD)/k(CH_3OH) = 16.6$  was observed for the photo-oxygenation, as shown in Table 3. The magnitude of 16.6 is much larger than that of 10 reported for  $D_2O-CD_3OD$ ,<sup>8</sup> but is as

Table 3. Effects of solvent deuteration on the rate of dye-sensitized photo-oxygenation of 3-methyl-1,2cyclohexanedione (1a)<sup>4</sup>

| Solvent            | Sensitizer  | Relative rate |
|--------------------|-------------|---------------|
| CH <sub>3</sub> OH | Rose Bengal | 1             |
| CHJOD              | Rose Bengal | 2.5           |
| CD,OD              | Rose Bengal | 16.6          |

\*[1a] =  $1.0 \times 10^{-4}$  M; [Rose Bengal] =  $5.0 \times 10^{-6}$  M; 30°.

large as that of 15.6–19.9 recently reported for deuterated acetone, acetonitrile, benzene and chloroform.<sup>9</sup> The results from both the quenching and the solvent deuteration effects strongly support the involvement of singlet oxygen in the dye-sensitized photo-oxygenation of 1a.

Dye-sensitized photo-oxygenation of 1,2-cyclohexanedione (1b)

The results, shown in Table 4, indicate that the product yields are highly dependent on the reaction conditions, such as temperature, sensitizer and solvent. A striking temperature dependence of product



distribution is observed in the reaction with Rose Bengal in MeOH, whereby, at 40°, aldehydic acid (2b) and its derivatives, 7 and 8, are produced in a combined yield of 72%, together with the formation of methyl 5carboxy-2-hydroxypentanoate (3b) in 3% yield, whereas at 0° the former decreases to 33% yield and the latter increases to 28%. A similar trend, though to a lesser extent, is observed in the reaction with methylene blue.<sup>‡</sup> The temperature-dependent formations of 2b and 3b are best accounted for in terms of nucleophilic trapping of an endoperoxide intermediate,

<sup>‡</sup> It remains unclear why the product distribution in the reaction with Rose Bengal is different from that with methylene blue.

|                   |                 |            |          | Temperature | Time | •          | Yield (% | 3  | Gas analysis (%) <sup>b</sup> |    |     |  |
|-------------------|-----------------|------------|----------|-------------|------|------------|----------|----|-------------------------------|----|-----|--|
| Quencher          | [Quencher]/[1a] | Sensitizer | Solvent  | (°)         | (hr) | 2 <b>a</b> | 3a 🕺     | 1a | 02                            | cò | CO2 |  |
| Dabco             | 0               | RB         | MeOH     | 0           | 5    | 91         | 2        | 0  | 96                            | 87 | 0   |  |
|                   | 1.0             |            |          |             |      | 49         | 1        | 15 |                               | _  |     |  |
|                   | 2.0             |            |          |             |      | 41         | 3        | 34 | _                             | _  |     |  |
|                   | 4.0             |            |          |             |      | 22         | 3        | 52 |                               |    |     |  |
|                   | 10.0            |            |          |             |      | 9          | 0        | 71 | 21                            | 7  | 0   |  |
|                   | 4.0             | MB         | MeOH     | 0           | 5    | 19         | 0        | 58 | 25                            | 15 | 0   |  |
| NaN <sub>3</sub>  | 0.5             | RB         | MeOH     | 35          | 5    | 1          | 0        | 79 | 7                             | 7  | 0   |  |
|                   | 0.5             | MB         | MeOH     | 35          | 5    | 1          | 0        | 76 | 4                             | 4  | 0   |  |
| $\beta$ -Carotene | 0               | RB         | Pyridine | 0           | 5    | 80         | _        | 0  | 77                            | 83 | 3   |  |
|                   | 0.0038          |            | -        |             |      | 34         |          | 35 | 28                            | 34 | 0   |  |
|                   | 0.01            |            |          |             |      | 17         | _        | 53 | —                             |    | _   |  |
|                   | 0.01            | MB         | Pyridine | 0           | 5    | 40         | -        | 38 | —                             | —  | _   |  |

Table 2. Quenching of dye-sensitized photo-oxygenation of 3-methyl-1,2-cyclohexanedione (1a)

\* RB, Rose Bengal; MB, methylene blue.

<sup>b</sup>O<sub>2</sub> absorbed, CO and CO<sub>2</sub> evolved.

<sup>&</sup>lt;sup>†</sup> From the competition between 1a and 2,3-dimethyl-2butene described in the Experimental, we can estimate a rate constant of  $4 \times 10^7 \, M^{-1} \, s^{-1}$  for the reaction of 1a with singlet oxygen.<sup>1b</sup> Since the rate of quenching of singlet oxygen by Dabco is reported to be 8.9 × 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup> in MeOH, <sup>7</sup> it is not incomprehensible that a large excess of Dabco is needed to suppress the photo-oxygenation of 1a. Moreover, Dabco as a base is expected to activate 1a by forming a hydrogen bond with the enol hydrogen.

|         |             | Temperature | Time |    |            | Yiel | Gas analysis (%) <sup>b</sup> |    |    |     |    |     |
|---------|-------------|-------------|------|----|------------|------|-------------------------------|----|----|-----|----|-----|
| Solvent | Sensitizer* | (°)         | (hr) | 2b | <b>7</b> ° | 8    | 36                            | 9⁴ | 1b | 02  | có | ČO2 |
| MeOH    | RB          | 40          | 13   | 62 | 10         | 0    | 3                             | 0  | 0  | 137 | 62 | 4   |
|         |             | 30          | 8    | 42 | 8          | 3    | 6                             | 1  | 14 |     | -  | —   |
|         |             | 0           | 13   | 28 | 3          | 2    | 28                            | 1  | 7  | 76  | 22 | 4   |
|         |             | - 70        | 24   | 15 | 1          | 3    | 21                            | 1  | 25 | -   | _  |     |
|         | MB          | 35          | 10   | 8  | 18         | 4    | 35                            | 1  | 0  | 100 | 10 | 8   |
|         |             | 30          | 10   | 9  | 23         | 7    | 33                            | 1  | 0  |     |    |     |
|         |             | 0           | 12   | 7  | 11         | 3    | 49                            | 1  | 0  | _   | _  |     |
|         |             | -70         | 24   | 15 | 11         | 5    | 32                            | 2  | 9  |     |    |     |
| EtOH    | RB          | 0           | 12   | 35 | 15         | 2    | 17                            | 0  | 0  | 87  | 27 | 2   |
| McCN    | MB          | 40          | 3    | 33 |            | 9    | _                             | 1  | 34 |     | _  |     |
|         |             | 40          | 9    | 53 |            | 10   | _                             | 4  | 0  | 123 | 63 | 12  |
|         |             | 0           | 3    | 48 | -          | 5    |                               | 4  | 12 |     | _  | _   |
|         |             | 0           | 6    | 19 | _          | 51   | _                             | 4  | 0  | _   | —  | _   |
|         |             | Ó           | 13   | 10 |            | 59   | _                             | 3  | 0  | 150 | 50 | 7   |

Table 4. Dye-sensitized photo-oxygenation of 1,2-cyclohexanedione (1b)

\* RB, Rose Bengal; MB, methylene blue.

 $^{b}O_{2}$  absorbed, CO and CO<sub>2</sub> evolved.

<sup>e</sup> In MeOH, R' = Me; in EtOH, R' = Et.

<sup>d</sup> In MeOH, R' = Me; in EtOH, R' = Et; in MeCN, R' = H.

**5b**, by MeOH (Scheme 1). At higher temperatures, the lifetime of **5b** will be shorter, permitting the trapping to a lesser extent. On the other hand, the trapping seems to be suppressed by the decreased nucleophilic reactivity of MeOH at  $-70^{\circ}$ . In accord with this, **1a** gives **3a** only in 0–5% yields, as shown in Table 1, probably owing to a steric hindrance due to the neighbouring Me group.

With acetonitrile as solvent, an unusual phenomenon is observed: at 40°, the yield of glutaric acid (8)† is 9-10%, irrespective of the reaction time (3-9 hr) while, at 0°, the yield of 8 increases from 5% to 59% as the reaction time increases from 3 to 13 hr.

The formation of adipic acid or monomethyl adipate (9), although in low yields (1-4%), deserves attention particularly since they are considered to be formed from the non-enolized dione, 1b, via free radical species produced photochemically.<sup>11</sup> Since the keto-enol equilibrium for 1b has a constant, K, equal to 1 in water,<sup>12</sup> it seems likely that an appreciable amount of the keto form is present in MeOH.<sup>‡</sup>

<sup>†</sup>The conversion of —CHO to —COOH by irradiation under oxygen has been reported.<sup>10</sup>

 $\pm$  Since the C—C double bond of 1a is stabilized by the methyl group, the keto content of 1a is expected to be so small that  $\alpha$ -methyladipic acid is not formed.

Table 5 includes the results for the quenching of dyesensitized photo-oxygenation of 1,2-cyclohexanedione (1b). Apparently, the formation of 2b is effectively suppressed by the addition of a quencher, but the formation of 9 is enhanced, indicating that singlet oxygen is involved in the former§ while other active species are involved in the latter.

# Reactivity of the enols, 1, toward singlet oxygen

Replacement of an olefinic H of 1b with a Me group increases the reaction rate by a factor of ca 3, as estimated from the reaction times for 1a and 1b in Tables 1 and 4. This factor of 3 is considerably smaller than that of 20 observed for the ene reaction of cyclohexenes with singlet oxygen.<sup>1b</sup> On the other hand, we can compare the reactivities of the enols, 1, toward singlet oxygen with those of substituted olefins in two ways. One is the intramolecular competition as realized in the enols 1c-e substituted with (Z)-2-pentenyl, (E)-2pentenyl, or 2-pentynyl group. Singlet oxygen has been found to react only with the enol double bond while the

§ We have tried to determine the solvent deuteration effect on the reaction of 1b. However, we have obtained an anomalous result that 1b decomposed faster than 1a under the reaction conditions used.

Table 5. Quenching of dye-sensitized photo-oxygenation of 1,2-cyclohexanedione (1b) in MeOH

| Quencher          |             | Temperature | Time |    |                | Yield (%) |    |                      |    | Gas analysis (%)° |    |     |
|-------------------|-------------|-------------|------|----|----------------|-----------|----|----------------------|----|-------------------|----|-----|
| ([quencher]/[1b]) | Sensitizer* | (°)         | (hr) | 2Ь | 7 <sup>6</sup> | 8         | 3b | 9 <sup>6</sup>       | 1b | O2                | ĊÒ | CO2 |
| _                 | RB          | 40          | 13   | 62 | 10             | 0         | 3  | 0                    | 0  | 137               | 62 | 4   |
| Dabco<br>(10.0)   | RB          | 40          | 13   | 5  | 0              | 1         | 0  | 27 (14) <sup>d</sup> | 18 | 43                | 4  | 2   |
| NaN <sub>3</sub>  | RB          | 35          | 12   | 3  | 0              | 6         | 0  | 1 (21) <sup>d</sup>  | 34 | 7                 | 1  | 0   |
| (0.5)             | MB          | 35          | 13   | 0  | 0              | 0         | 0  | 10 (48) <sup>4</sup> | 0  | 33                | 3  | 4   |

\*RB, Rose Bengal; MB, methylene blue.

 $^{b}R' = Me.$ 

 $^{\circ}O_2$  absorbed, CO and CO<sub>2</sub> evolved.

<sup>d</sup> The values in parentheses are for unidentified intractable material and calculated by assuming the molecular weight equal to 1b.



disubstituted alkene or alkyne remained intact.<sup>5</sup> The other is the intermolecular competition between 1a and 2,3-dimethyl-2-butene (TME), which is one of the most reactive substrates for the singlet oxygen enereaction.<sup>16</sup> Here, 1a has been found to react with singlet oxygen in a rate comparable to that for TME. Such a high reactivity of the enol, 1a, will find many applications in organic syntheses, as exemplified by the jasmine lactone synthesis.<sup>5</sup> Thus, it can be concluded that the C-C double bond of the enol, 1, is considerably activated by the electron-releasing OH group rather than deactivated by the electron-withdrawing CO group.

# Hydroperoxide, 4, endoperoxide, 5, and dioxetane, 6, as intermediates

The enol, 1, may react with singlet oxygen in a dual fashion; the ene reaction to form a hydroperoxide, 4, and the 1,2-cycloaddition to form a dioxetane, 6. The latter path can be ruled out or should be negligible for 1a since carbon dioxide was not detected at all or detected only in small amounts (Table 1). For 1b, carbon dioxide was produced in somewhat larger amounts, up to 12% (Table 4). However, this does not mean that dioxetane, 6b, is formed directly from 1b by the 1,2-cycloaddition, since methyl ether, 1f, did not form a dioxetane with singlet oxygen.<sup>†</sup> Thus the



dioxetane 6 is most likely formed from 4 in competition with the formation of 5, and converted to 2 via  $\alpha$ -keto acid with the evolution of carbon dioxide<sup>+</sup> (Scheme 1).

The main path should be the formation of endoperoxide, 5, as intermediate which may give 2 with the evolution of carbon monoxide. It is quite natural that the hydroperoxide, 4, tends to cyclize to the less strained five-membered endoperoxide, 5, rather than to close to the four-membered dioxetane, 6.

We have tried unsuccessfully to detect 5 by measuring the NMR spectra at low temperatures.§ The trapping with MeOH to give 3, of course, provides strong support for the intermediacy of 5. The fact that the trapping is less favourable in EtOH than in MeOH (Table 4) is consistent with the nucleophilic attack by the solvent molecules at the carbonyl carbon of endoperoxide, 5.

## EXPERIMENTAL

All b.ps are uncorrected. IR spectra were recorded with a JASCO A-102 spectrometer. <sup>1</sup>H-NMR spectra were obtained on a JEOL PMX 60 SI spectrometer at 60 MHz and <sup>13</sup>C-NMR spectra were obtained on a JEOL FX-100 spectrometer at 25 MHz. TMS was used as internal standard. Bulb-to-bulb distillation was performed by using a Shibata glass tube oven GTO-250. Elemental analyses were conducted by Mr. Eiichiro Amano of our laboratory.

Compounds 1a and 1b were conveniently prepared according to the method reported earlier.<sup>16</sup> Compound If was prepared according to the method reported in the lit.<sup>17</sup> 2,3-Dimethyl-2-butene from Aldrich was used as received. MeOH, EtOH, MeCN, pyridine and CHCl<sub>3</sub> were purified by distillation after treatment with Mg, Mg, CaH-P<sub>2</sub>O<sub>3</sub>, KOH pellets-BaO and CaCl<sub>2</sub>, respectively. Rose Bengal was from Chroma-Gesellschaft and methylene blue as trihydrate was from Nakarai Chemicals. Both were used as received. Dabco and NaN<sub>3</sub> from Nakarai Chemicals and  $\beta$ -carotene from Merck were also used as received. Deuterated methanols (CH<sub>3</sub>OD, d ≥ 99%; CD<sub>3</sub>OD, d ≥ 99.5%) were from CEA of France.

Dye-sensitized photo-oxygenation of 1,2-cyclohexanediones (1a,b). A soln of 1 (2 mmol) and sensitizer (3 mg) in the solvent (10 ml) was irradiated with a 100 W tungsten-halogen lamp (no filter) under  $O_2$ . The soln was stirred magnetically. Absorption of  $O_2$  and evolution of CO were followed by both manometry and GC. After the reaction was complete, the solvent was evaporated and the residual oil checked using NMR spectra. Then the oil was treated with diazomethane in ether and distilled (up to 180° (2 mmHg)) to give a colourless oil, which was analysed by GLC. Analytical samples were obtained by preparative GLC, TLC, or HPLC.

Gas analyses. The analyses were performed by using GC with molecular sieves 5A for  $O_2$  and CO and with silica gel for  $O_2$  and  $CO_2$ .

Quenching experiments. The photo-oxidation was carried out in the presence of a quencher in the manner similar to that described above. Quenchers (Dabco and NaN<sub>3</sub>) were then removed from the reaction mixture by washing with dil aq HCl or water.

Measurement of photo-oxygenation rates in CH<sub>3</sub>OH, CH<sub>3</sub>OD and CD<sub>3</sub>OD. A methanolic soln containing 1 (1.0  $\times 10^{-4}$  M) and Rose Bengal (5.0  $\times 10^{-5}$  M) was saturated with O<sub>2</sub>. Then the soln was transferred to a cuvette and irradiated with a 100 W tungsten-halogen lamp (no filter). Rates of photo-oxygenation of 1 were followed by monitoring the decrease in the absorption maximum at 270 nm with a Hitachi model 200-10 spectrometer. A good pseudo-first-order kinetics was found to hold up to more than three half-life periods. The rate constant was reproducible within 10%. Absorption spectra from 500 to 590 nm were taken to ensure that the amount of Rose Bengal in each run was identical. The optical density was found to decrease by ca 10% during irradiation.

Competition between 1a and 2,3-dimethyl-2-butene (TME). Competition was carried out using a soln of 1a (2 mmol), TME (2 mmol) and RB (3 mg) in MeOH (10 ml). The soln was irradiated at 0° for 3 hr under  $O_2$ . The MeOH was then removed in vacuum and the residual oil analysed with <sup>1</sup>H- and <sup>13</sup>C-NMR spectra. The oil contained 1a, 2a and 3-hydroperoxy-2,3-dimethyl-1-butene in a mole ratio of 0.7:1.2:1 as calculated by the integrated intensities of <sup>1</sup>H-NMR signals.

5-Oxohexanoic acid (2a). B.p. 150–160° (1 mmHg); IR  $\nu_{max}^{nest}$ 3700–2300, 1735, 1710 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  1.6–2.1 (2H, m), 2.15(3H, s), 2.37(2H, t, J = 6 Hz), 2.55(2H, t, J = 7 Hz), 9.4(1H, br s); <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$  18.2(t), 29.3(q), 32.5(t), 41.9 (t), 177.5 (s), 208.9 (s).

Methyl 5-oxohexanoate. B.p. 100° (2 mmHg); IR vmax 1737,

<sup>&</sup>lt;sup>†</sup>The starting ether, 1f, was recovered intact.

 $<sup>\</sup>ddagger$  The photosensitized decarboxylation of  $\alpha\text{-keto}$  acid has been reported.  $^{13}$ 

<sup>§</sup> A five-membered endoperoxide similar to 5 was proposed as an unstable intermediate in the dye-sensitized photooxygenation of quercetin or 3-hydroxyflavones<sup>2bx</sup> and in the biological degradation of quercetin by quercetin dioxygenase.<sup>14</sup> Recently, we have reported that 1 is also dioxygenated by cupric ion as catalyst, possibly through 5, to give 2 and 3.<sup>15</sup>

1718 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  1.65–2.1 (2H, m), 2.12 (3H, s), 2.33 (2H, t, J = 6 Hz), 2.50 (2H, t, J = 7 Hz), 3.65 (3H, s). (Found : C, 58.48; H, 8.49%. Calc for C<sub>7</sub>H<sub>12</sub>O<sub>3</sub> (144.2): C, 58.32; H, 8.39%.)

Methyl 5-carboxy-2-methyl-2-hydroxypentanoate (3a). The <sup>1</sup>H-NMR spectrum for the crude photo-oxygenation product of 1a indicated the presence of the ester 3a in 2-5% yields, as shown in Table 1. Isolation of 3a was realized by using a larger amount (3.5 g) of 1a for the photo-oxygenation. The crude product was separated by LC [Wako gel, C 200, hexane-acetone-ether (6:2:1)] to give 70 mg of crude 3a. <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  1.39 (3H, s), 1.5-1.9 (4H, m), 2.1-2.5 (2H, m), 3.74 (3H, s), 7.9 (br s).

Methyl 5-methox ycarbonyl-2-methyl-2-hydrox ypentanoate. The crude 3a was esterified with diazomethane. The product was distilled and purified by preparative GLC. B.p.  $150^{\circ}$  (2 mmHg); IR  $v_{max}^{ast}$  3550, 1740 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  1.39 (3H, s), 1.5–1.9 (4H, m), 3.0 (1H, br s), 3.64 (3H, s), 3.76 (3H, s); <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$  19.3 (t), 26.1 (q), 33.9 (q), 39.3 (t), 74.4 (s), 51.5 (q), 52.8 (q), 173.7 (s), 177.4 (s). (Found : C, 52.74; H, 7.79%. Calc for C<sub>9</sub>H<sub>16</sub>O<sub>5</sub> (204.2): C, 52.93; H, 7.90%.)

5-Oxopentanoic acid (2b). The crude product was shortcolumn chromatographed over Florisil. <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$ 1.7-2.2 (2H, m), 2.3-2.8 (4H, m), 8.0 (1H, br s), 9.78 (1H, t, J = 1 Hz); <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$  16.9 (t), 32.6 (t), 42.5 (t), 177.9 (s), 202.3 (d).

Methyl 5-oxopentanoate. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 1.8-2.1 (2H, m), 2.2-2.6 (4H, m), 3.66 (3H, s), 9.79 (1H, t).

Methyl 5,5-dimethoxypentanoate. <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  1.6– 1.8 (4H, m), 2.2–2.45 (2H, m), 3.31 (6H, s), 3.67 (3H, s), 4.32 (1H, t).

Methyl 5-carboxy-2-hydroxypentanoate (3b). From the crude reaction product, 3b was isolated by HPLC [Yanapack SA-1, hexane-ether (1:3)]. <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  1.5-1.9 (4H, m), 2.15-2.6 (2H, m), 3.78 (3H, s), 4.23 (1H, m), 4.5 (br s); <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$  20.2 (t), 33.3 (t), 33.4 (t), 52.5 (q), 70.1 (d), 175.2 (s), 178.0 (s).

 $\begin{array}{l} Methyl 5-methox ycarbonyl-2-hydrox ypentanoate. B.p. 150-160° (1 mmHg); IR v_{max}^{nest} 3450, 1730 cm ^{-1}; ^{1}H-NMR (CDCl_3)\delta 1.4-1.9 (4H, m), 2.1-2.5 (2H, m), 3.65 (3H, s), 3.75 (3H, s), 4.23 (1H, m); ^{13}C-NMR (CDCl_3) \delta 20.4 (t), 33.5 (2C, t), 51.6 (q), 52.4 (q), 70.2 (d), 173.9 (s), 175.3 (s); Mass (CI, NH_3) 191 [MH]^+, 208 [MNH_4]^+. \end{array}$ 

3-Hydroperoxy-2,3-dimethyl-1-butene. <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$ 1.36 (6H, s), 1.81 (3H, s), 4.96 (2H, m); <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$ 18.5 (q), 23.3 (2C, q), 84.1 (s), 111.7 (t), 148.2 (s).

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