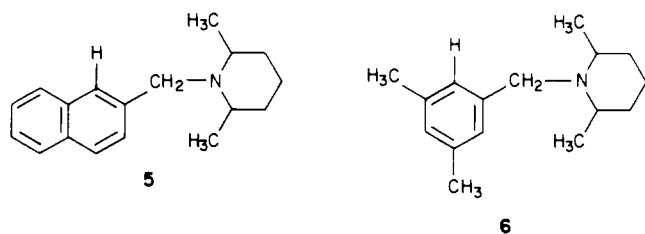


**4** gave **3h** and **4h** but also varying amounts of tele substitution products **5** and **6**, respectively. Data from some representative experiments are set forth in Table I.



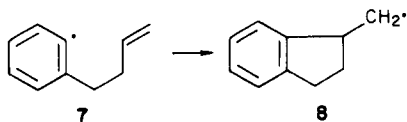
Concerning the first four entries, we note that the presence of di-*tert*-butyl peroxide causes the yield of **3h** from **3i** to increase from 37% to 63% while the presence of 1,1-diphenylethene or azobenzene lowers it respectively to 18% or 10%. Inasmuch as di-*tert*-butyl peroxide is a radical source and the other two added substances are radical and/or electron traps, these data fulfill expectations for a radical chain mechanism.

The four entries for substrate **3c** in Table I show some of the same features, but in muted form: a small augmentation of dehalogenation yield by di-*tert*-butyl peroxide, and a modest diminution by 1,1-diphenylethene. Tetraphenylhydrazine causes an increase in dehalogenation yield; conceivably it acts as a source of radicals (by homolysis to Ph<sub>2</sub>N<sup>•</sup>). It is noteworthy that the yield of substitution product **5** wanes as the yield of **3h** waxes.

The four experiments in Table I concerning **4i** show it to be less reactive than **3i** in dehalogenation. Again acceleration by di-*tert*-butyl peroxide is evident. The crown ether<sup>12</sup> 12-crown-4, which chelates Li<sup>+</sup> well, strongly inhibits deiodination.

The four experiments on **4b** manifest qualitatively the same effects as just discussed for **4i**, except that some tele substitution to form **6** now occurs.

Thanks to Beckwith and co-workers,<sup>13,14</sup> we have available another tool to probe radical character, namely, the propensity of the *o*-(3-butenyl)phenyl radical (**7**), to cyclize to 1-indanyl-methyl radical (**8**). Reaction of *o*-(3-butenyl)iodobenzene<sup>15</sup> with



**2** in 2,6-dimethylpiperidine solution (24 h at room temperature) afforded 28% of 1-methylindan as well as 27% of 3-butenylbenzene, affirming the intermediacy of **7**. But the chlorine analogue, *o*-(3-butenyl)chlorobenzene, under the same conditions gave 3-butenylbenzene (10%) free of cyclization product. Thus a nonradical mechanism is indicated for it.

Dehalogenations of **3i** and of **3c**, through the action of **2** in *N*-deuterio-2,6-dimethylpiperidine solution, afforded **3h** free of deuterium at C-1 but deuterated in the methyl group (owing to base-catalyzed hydron exchange). These results inveigh against any mechanism that would involve 1-lithio-2-methylnaphthalene or the 2-methyl-1-naphthyl anion as an intermediate.

Our experimental findings are concordant with expectations from the mechanism of Scheme I insofar as aryl iodides are concerned. One aryl chloride result is contraindicative of that mechanism, while others are weakly in accord with it. We think that some nonradical mechanism of hydrodechlorination may experience an overlay of reaction according to Scheme I when a good source of radicals is present.

The remarkable retardation of radical chain dehalogenation by 12-crown-4 suggests that tight ion pairing if not actual covalent bonding with lithium is essential if some unidentified step(s) is to occur.

(12) Formally, 12-crown-4 is 1,4,7,10-tetraoxacyclododecane.

(13) Beckwith, A. L. J.; Gara, W. B. *J. Chem. Soc., Perkin Trans. 2*, 1975, 795.

(14) Meijs, G. F. Ph.D. Thesis, University of Adelaide, Australia, 1981.

(15) The *o*-(3-butenyl)iodobenzene was prepared by Dr. G. F. Meijs, to whom we are grateful.

Our observations furnish only meager indications of how tele substitution to form **5** or **6** occurs: In debromination of **3b** in *N*-deuterio-2,6-dimethylpiperidine at reflux (16 h), besides **3h** (48%) free of deuterium at C-1 we obtained 29% of **5** which carried deuterium at C-1. Data in Table I suggest the mechanism to be of nonradical character.

### Metal Ion Complexation by Rhodium and Iridium Metallomacrocycles. The Preparation and X-ray Crystal Structures of

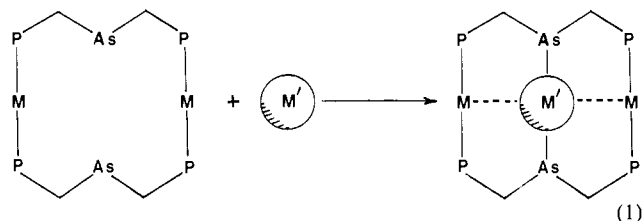
#### Rh<sub>2</sub>(CO)<sub>2</sub>Cl<sub>2</sub>(μ-Ph<sub>2</sub>PCH<sub>2</sub>As(Ph)CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub> and [Rh<sub>2</sub>Pd(CO)<sub>2</sub>Cl<sub>3</sub>(μ-Ph<sub>2</sub>PCH<sub>2</sub>As(Ph)CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>][BPh<sub>4</sub>]

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The diverse reaction chemistry that has developed around diphosphine-bridged, binuclear complexes has expanded our knowledge of metal-metal bonding, given insight into the interaction of small molecules with two metal centers, and provided models for species bound to catalytically active metal surfaces.<sup>1,2</sup> Polyfunctional phosphine ligands can be designed to produce more complex arrays of reactive metal centers which are expected to display multicenter metal-metal interactions and allow for multisite metal/small molecule bonding. The tripod ligand tris(diphenylphosphino)methane can stabilize or create new triangular arrays of metal centers<sup>3,4</sup> while bis[(diphenylphosphino)methyl]phenylphosphine<sup>5-9</sup> and 2,6-bis(diphenylphosphino)pyridine<sup>10</sup> can be used to place three or four rhodium ions into nearly linear arrays. With metal ions other than rhodium dpmp forms six-membered chelate rings which cannot, as yet, be opened up to give linear chain complexes with metal ions in close proximity.<sup>11</sup> Thus, to date, this class of ligands has not yielded complexes that contain linear, trinuclear arrays with any transition metals except rhodium. Here we describe the creation of metallomacrocycles **1** using the tridentate ligand bis(diphenylphosphinomethyl)phenylarsine (dpma) and the subsequent complexation, as shown in eq 1, of a third, different metal ion to form



new trinuclear species **2** in which the central metal differs from the outer two. This procedure extends the range of trinuclear chains by allowing different metal ions to be placed in the center of the chain. In order to form **1** we take advantage of the

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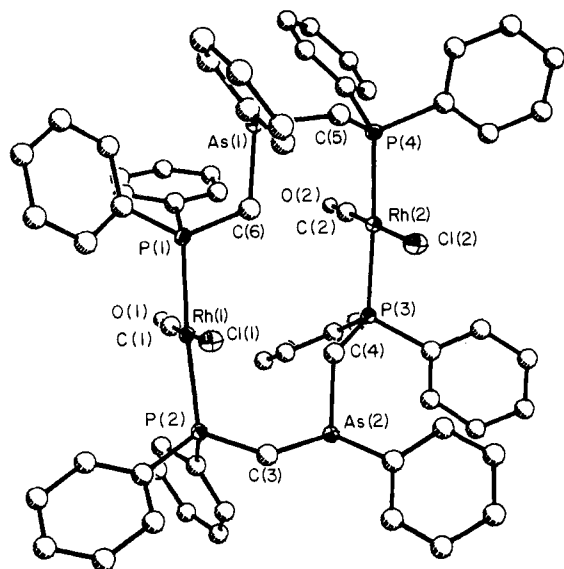
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**Figure 1.** Perspective drawing of  $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2$ . Selected interatomic distances: Rh(1)–P(1), 2.310 (1); Rh(1)–P(2), 2.341 (1); Rh(2)–P(3), 2.316 (1); Rh(2)–P(4), 2.326 (1); Rh(1)–Cl(1), 2.373 (1); Rh(2)–Cl(2), 2.381 (1); Rh(1)–C(1), 1.794 (5); Rh(2)–C(2), 1.808 (5) Å. Selected interatomic angles: P(1)–Rh(1)–P(2), 173.6 (1)°; P(3)–Rh(2)–P(4), 174.5 (1)°; P(1)–Rh(1)–Cl(1), 87.8 (1)°; P(1)–Rh(1)–C(1), 88.7 (2)°; P(2)–Rh(1)–C(1), 97.0 (2)°; P(2)–Rh(1)–Cl(1), 86.6 (1)°; P(3)–Rh(2)–Cl(2), 89.2 (1); P(3)–Rh(2)–C(2), 90.3 (2)°; P(4)–Rh(2)–Cl(2), 87.7 (1)°; P(4)–Rh(2)–C(2), 92.9 (1)°.

preference of metal ions to bind phosphorus rather than arsenic<sup>12,13</sup> and also utilize as M the  $\text{Rh}^1(\text{CO})$  and  $\text{Ir}^1(\text{CO})$  groups which preferentially bind phosphines in mutually trans orientations.<sup>14</sup> This step creates the macrocycle **1** in such a fashion that it is prepared to accept the second metal without forming polymers with different alignment of the trans bridging phosphines or mixtures with metal ions in different locations.

Bis[(diphenylphosphino)methyl]phenylarsine was prepared by the reaction between phenyldichloroarsine and 2 mol of (diphenylphosphino)methyl lithium–tetramethylethylenediamine<sup>15</sup> in tetrahydrofuran at  $-78^\circ\text{C}$  followed by evaporation, extraction with chloroform, and recrystallization from hot ethanol. The product was obtained in 67% yield: mp  $127\text{--}130^\circ\text{C}$ ;  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta -20.9$  ( $\text{CH}_2\text{Cl}_2$ ).

Treatment of dpma with  $1/2$  mol of rhodium dicarbonyl chloride dimer in toluene solution yields a precipitate of yellow crystals (77% yield) of  $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2$  (**3**):  $\nu(\text{CO})$  1978  $\text{cm}^{-1}$  (toluene);  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta$  24.7,  $^1J(\text{Rh},\text{P}) = 120$  Hz ( $\text{CH}_2\text{Cl}_2$ ). Similarly dpma reacts with  $\text{Ir}(\text{CO})_2\text{Cl}(p\text{-toluidine})$ <sup>16</sup> to form pale yellow  $\text{Ir}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2$  (**4**):  $\nu(\text{CO})$  1964  $\text{cm}^{-1}$  (toluene);  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta$  18.4 ( $\text{CH}_2\text{Cl}_2$ ). Neither preparation requires the high dilution techniques which are so commonly necessary in macrocycle synthesis. The structure of the rhodium compound **3** was determined by X-ray crystallography and is shown in Figure 1.<sup>17</sup> The molecule possesses two planar *trans*- $\text{Rh}(\text{CO})\text{ClP}_2$  units connected together through the bridging phosphines. The  $\text{Rh}\cdots\text{Rh}$  separation, 5.428 (2) Å, is too long to support any direct interaction

(12) Stability constant data indicate that the tendency of hard or class a metal ions to bind to group 15<sup>20</sup> donors follows the order  $\text{N} \gg \text{P} > \text{As} > \text{Sb}$  while soft or class b metal ions show the order  $\text{N} < \text{P} > \text{As} > \text{Sb}$ .<sup>13</sup> In either case phosphorus is expected to be a better donor than arsenic.

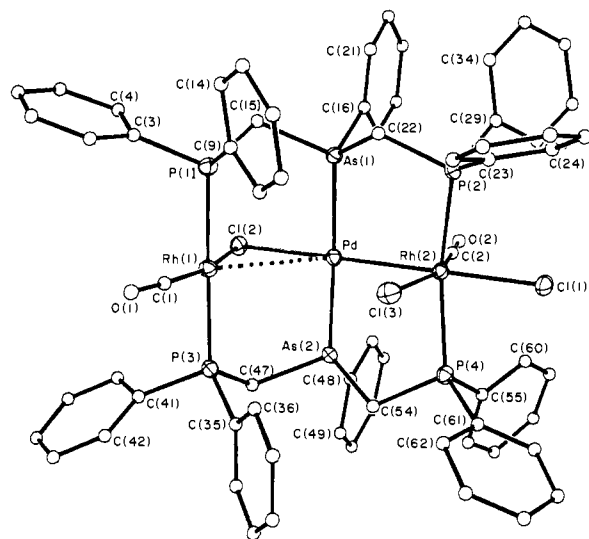
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(17) Yellow-orange crystals of  $\text{Rh}_2(\text{CO})_2\text{Cl}_2(\mu\text{-dpma})_2 \cdot \text{CH}_2\text{Cl}_2$  were grown by diffusion of ether into a dichloromethane solution of **3**. They belong to the space group *P1* (No. 2) with  $a = 12.731$  (2) Å,  $b = 12.849$  (2) Å,  $c = 20.024$  (2) Å,  $\alpha = 86.11$  (1)°,  $\beta = 83.01$  (1)°,  $\gamma = 75.00$  (1)°, at 140 K,  $Z = 4$ ,  $R = 0.036$ ,  $R_w = 0.034$  for 8144 reflections with  $I > 3\sigma(I)$  and 385 parameters.



**Figure 2.** Perspective drawing of the cation  $[\text{Rh}_2\text{Pd}(\text{CO})_2\text{Cl}_3(\mu\text{-dpma})_2]^+$ . Selected interatomic distances: Rh(2)–Pd, 2.699 (1) Å; Rh(1)–Pd, 3.166 (1); Pd–As(1), 2.379 (1); Pd–As(2), 2.384 (1); Pd–Cl(2), 2.440 (3); Rh(1)–P(1), 2.317 (3); Rh(1)–P(3), 2.310 (3); Rh(2)–P(2), 2.383 (3); Rh(2)–P(4), 2.370 (3); Rh(1)–C(1), 1.792 (14); Rh(1)–Cl(2), 2.408 (3); Rh(2)–Cl(1), 2.448 (3); Rh(2)–Cl(3), 2.389 (3); Rh(2)–C(2), 1.832 (14) Å. Selected interatomic angles: As(1)–Pd–As(2), 177.1 (1)°; P(1)–Rh(1)–P(3), 175.0 (1)°; P(3)–Rh(2)–P(4), 163.9 (1)°; Rh(2)–Pd–Rh(1), 126.8 (1)°; Rh(2)–Pd–Cl(2), 175.5 (1)°; Pd–Rh(2)–Cl(1), 175.0 (1)°; Cl(2)–Rh(1)–C(1), 165.8 (5)°; Pd–Cl(2)–Rh(1), 81.5 (1)°.

across the relatively empty cavity in the center of the molecule. The two arsenic lone pairs point away from the central cavity in the molecule but the conformational flexibility that renders the four phosphorus atoms equivalent in solution can allow for their reorientation so that the cavity can bind another metal ion.

Treatment of **3** with bis(benzonitrile)palladium(II) chloride in dichloromethane yields a deep red solution from which red crystals of  $[\text{Rh}_2\text{Pd}(\text{CO})_2\text{Cl}_3(\mu\text{-dpma})_2][\text{BPh}_4]$  (**5**) ( $\nu(\text{CO})$  1994  $\text{cm}^{-1}$  ( $\text{CH}_2\text{Cl}_2$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta$  19.1,  $J(\text{Rh},\text{P}) = 117$  Hz,  $\delta$  14.9,  $J(\text{Rh},\text{P}) = 84$  Hz;  $^{13}\text{C}$  NMR carbonyl groups  $\delta$  1 = 184.8,  $^1J(\text{Rh},\text{C}) = 62$  Hz,  $\delta$  2 = 184.0,  $^1J(\text{Rh},\text{C}) = 71$ ,  $^2J(\text{P},\text{C}) = 14$  Hz ( $\text{CH}_2\text{Cl}_2$ )) are obtained in 75% yield by precipitation with a methanolic solution of sodium tetraphenylborate. The iridium analogue **4** reacts similarly to form  $[\text{Ir}_2\text{Pd}(\text{CO})_2\text{Cl}_3(\mu\text{-dpma})_2][\text{BPh}_4]$  (**6**): yield, 88%;  $\nu(\text{CO})$  2012, 1974  $\text{cm}^{-1}$ ;  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta$  12.5,  $\delta$  2 = 17.8;  $^{13}\text{C}$  NMR  $\delta$  1 = 168.6,  $^2J(\text{C},\text{P}) = 12$  Hz,  $\delta$  2 = 163.0,  $^2J(\text{C},\text{P}) = 6.2$  Hz ( $\text{CH}_2\text{Cl}_2$ ).

The structure of the rhodium/palladium cation in **5** as determined by an X-ray diffraction study is shown in Figure 2.<sup>18</sup> The palladium ion is bonded to both arsenic atoms which are now turned inward with respect to the complex core. However, the palladium is asymmetrically positioned between the two rhodium ions. The Pd–Rh(2) distance, 2.699 (1) Å, is indicative of the presence of a Pd–Rh single bond,<sup>6</sup> whereas the Pd $\cdots$ Rh(1) separation (3.166 (1) Å) is longer and represents a much weaker interaction. The two rhodium ions are clearly in distinct environments. In essence a Pd–Cl bond has oxidatively added to Rh(2) to give a six-coordinate geometry about Rh(2).<sup>19</sup> On the other

(18) Red parallelepipeds of  $[\text{Rh}_2\text{Pd}(\text{CO})_2\text{Cl}_3(\mu\text{-dpma})_2][\text{BPh}_4] \cdot 2\text{CH}_2\text{Cl}_2 \cdot (\text{C}_2\text{H}_5)_2\text{O}$  were grown by diffusion of ethyl ether into a dichloromethane solution of **5**. They belong to the monoclinic space group *P2<sub>1</sub>/n*, a nonstandard setting *P2<sub>1</sub>/c* (No. 14), with  $a = 20.354$  (3) Å,  $b = 14.494$  (3) Å,  $c = 32.987$  (5) Å,  $\beta = 104.65$  (1)° at 140 K,  $Z = 4$ ,  $R = 0.071$ ,  $R_w = 0.060$  for 11021 reflections with  $I > 2\sigma(I)$  and 535 parameters.

(19) For other cases of oxidative addition of Pd–Cl bonds to Rh(1), see: Farr, J. P.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1983**, *22*, 1229.

(20) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become group 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III  $\rightarrow$  3 and 13.)

hand the surroundings of Rh(1) have been much less altered from their state in **1**.

The structural data in Figures 1 and 2 clearly display the nature of the complexes involved in eq 1. The dpma ligand is sufficiently flexible so that it can accommodate a range of metal-metal interactions within polynuclear units. Further work is under way to identify the range of metal ions which can be placed within the central cavity of **1** and **2** and to construct other metallo-macrocycles using dpma and related ligands.

**Acknowledgment.** We thank the National Science Foundation (CHE 8217954) for financial support and Dow Corning for a fellowship to P.E.R.

**Supplementary Material Available:** Tables of atomic coordinates and thermal parameters for **3** and **5** (5 pages). Ordering information is given on any current masthead page.

### Sensitized Photooxygenation. 1. Reaction of Singlet Oxygen with 3,4-Dihydro-6-methyl-2H-pyran-5-carboxylic Acid Ethyl Ester. Isolation of Hydroperoxides and Evidence of the Transformation of One of Them to Dioxetane<sup>1</sup>

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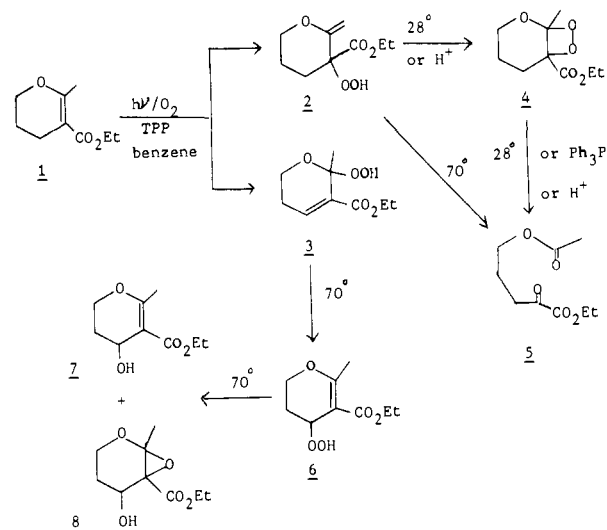
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The photooxygenation of alkenes and enol ethers has been the subject of much interest.<sup>2</sup> Enol ethers that cannot form hydroperoxides furnish cleavage products derived from dioxetanes.<sup>3</sup> Enol ethers having accessible allylic hydrogen react with singlet oxygen to yield allylic hydroperoxides, together with dioxetane, as primary products,<sup>2,4</sup> which in a lot of cases are not isolated due to thermal instability. The 3,4-dihydro-2H-pyran systems have been under active investigations.<sup>5</sup> We wish to report our preliminary findings in the photooxygenation of 3,4-dihydro-6-methyl-2H-pyran-5-carboxylic acid ethyl ester (**1**). Compound **1** is a novel and versatile system with stabilizing substituents. Two stable hydroperoxides **2** and **3** are isolated as primary products by normal column chromatography at room temperature. Thermal or acid-catalyzed Hock cleavage<sup>2,6</sup> of **2** proceeds via a dioxetane<sup>7</sup> intermediate **4** instead of the Criegee mechanism.<sup>8</sup> Hydroperoxide

**3** undergoes thermal 1,3-allylic rearrangement<sup>9</sup> to form 4-OOH **6**. Altogether six monoxygenated intermediates and products are isolated from the reaction of **1** with singlet oxygen.

Photooxygenation of **1**<sup>10</sup> using TPP as sensitizer at room temperature in benzene gave a mixture of two intermediates. The mixture was unstable upon prolonged irradiation, thermal decomposition, or prolonged storage at -5 °C. Purification of the mixture as soon as **1** was totally consumed led to the isolation of two stable hydroperoxides,<sup>11</sup> 5-OOH **2** and 6-OOH **3** (~1:9)<sup>12</sup> in 90% yield. Pure hydroperoxides can be stored in benzene solution at -5 °C for >2 weeks.

When the thermal Hock cleavage of pure **2** was followed by NMR spectrometry<sup>13</sup> in CCl<sub>4</sub> at 70 °C, no apparent intermediate species could be detected. After 1 h, **2** had decomposed completely to the "dioxetane mode" cleavage product, keto ester **5**. But when



the decomposition was followed at 28 °C in CCl<sub>4</sub>, a new intermediate **4** was clearly detected and isolated.<sup>14</sup> The structure of **4** was readily ascertained from its spectral data to be the dioxetane. It took 13 h for **2** to rearrange completely to **4**, at which time some keto ester **5** was also detectable. Dioxetane **4** slowly decomposed to **5** within 24 h. If **4** was decomposed at 70 °C, it was converted to **5** immediately. This is probably the reason why in the decomposition of **2** at 70 °C, no dioxetane was detected. When a solution of **4** in CCl<sub>4</sub> was treated with Ph<sub>3</sub>P<sup>4</sup> (>90%) was formed immediately. If 1 drop of concentrated HCl<sup>8</sup> was added to **4** in CCl<sub>4</sub>, **4** was completely decomposed to **5** in 30 min. Acid-catalyzed Hock cleavage of 5-OOH **2** was carried out by adding 1 drop of concentrated HCl to **2** in CCl<sub>4</sub> at room temperature. After 10 min, dioxetane **4** and keto ester **5** were present together with **2** in ~1:1:1 ratio. The mixture was completely converted to **5** after 30 min.

The above phenomena led to the conclusion that in our system, both thermal and acid-catalyzed Hock cleavage of allylic hy-

\* Also spelled as Yu-Yi Chen and Xiao-Guang Liang, respectively, in China.

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(10) Preparation: Ploner, K. J.; Wamhoff, H.; Korte, F. *Chem. Ber.* **1967**, *100*, 1675. Chan, Y. Y. et al., unpublished results. Photooxygenation conditions: 0.3-0.4 M **1**, 3 × 10<sup>-4</sup> M TPP; irradiated with a 500-W tungsten-halogen lamp, operated at 180 V, for 9 h, with oxygen bubbling; without light, oxygen, or sensitizer, no reaction was observed.

(11) Structures of all new compounds were consistent with their analytical data. Analytical instrumentation and data in more detail are available as supplementary materials. All compounds show distinct GC peaks. The MS (CI) spectra for all six monoxygenated products, **2-6** and **8** have peaks at *m/e* 203 (M + 1). NMR δ (characteristic peaks for 6-CH<sub>3</sub> in CCl<sub>4</sub>): **1**, 2.1; **3**, 1.7; **4**, 1.57; **5**, 2.05; **6**, 2.3; **7**, 2.3; **8**, 1.54. **2**, 4.15, 4.65 (2d, =CH<sub>2</sub>). The three hydroperoxides all have OOH signals at 9.0, 8.7, and 9.1, respectively.

(12) The directing effect of the ester group is similar to that reported by Ensley; Ensley, H. E.; Balakrishnan, P.; Ugarkar, B. *Tetrahedron Lett.* **1983**, 5189 and references cited therein.

(13) <sup>1</sup>H NMR: 60 MHz, Varian EM360L.

(14) Dioxetane **4** could be isolated from the prolonged irradiation mixture and also from the mixture on storing at -5 °C.