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 metallomacrocycles using dpma and related ligands.

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[1]

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The photooxygenation of alkenes and enol ethers has been the subject of much interest.[2] Enol ethers that cannot form hydroperoxides furnish cleavage products derived from dioxetanes.[3] Enol ethers having accessible allylic hydrogen react with singlet oxygen to yield allylic hydroperoxides, together with dioxetane, as primary products,[2,4] 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.[5] 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[2,6] of **2** proceeds via a dioxetane[7] intermediate **4** instead of the Criegee mechanism.[8] Hydroperoxide

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[†] Also spelled as Yu-Yi Chen and Xiao-Guang Liang, respectively, in China.

(1) Presented in part at the 3rd National Meeting of Photochemistry, Guilin, China, Oct 15–21, 1984.

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3 undergoes thermal 1,3-allylic rearrangement[9] to form 4-OOH **6**. Altogether six monooxygenated intermediates and products are isolated from the reaction of **1** with singlet oxygen.

Photooxygenation of **1**[10] 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,[11] 5-OOH **2** and 6-OOH **6** ($\sim$1:9)[12] 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[13] in CCl_4 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
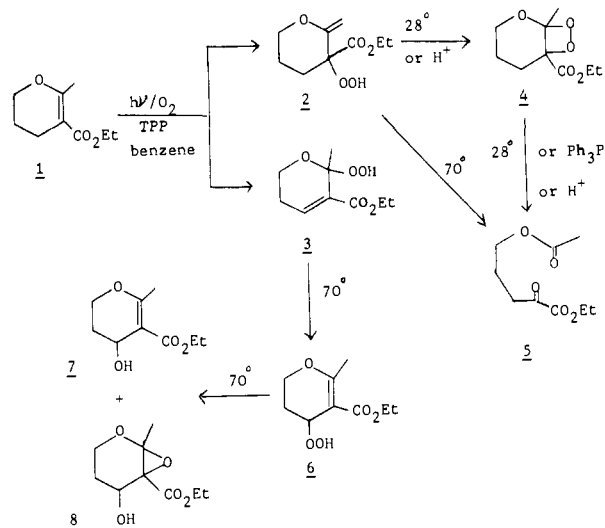
the decomposition was followed at 28 °C in CCl_4, a new intermediate **4** was clearly detected and isolated.[14] The structure of **4** was readily ascertained from its spectral data to be the dioxetane. It took 13 h for **2** to rearrange completely to **4**, at which time some keto ester **5** was 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_4 was treated with Ph_3P[4] **5** (>90%) was formed immediately. If 1 drop of concentrated HCl[8] was added to **4** in CCl_4, **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_4 at room temperature. After 10 min, dioxetane **4** and keto ester **5** were present together with **2** in $\sim$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-

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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^{-4}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 monooxygenated products, **2–6** and **8** have peaks at m/e 203 (M + 1). NMR δ (characteristic peaks for 6-CH_3 in CCl_4): **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_2). 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) ¹H 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.

droperoxide **2** proceeded via a dioxetane intermediate. Acid-catalyzed cleavage occurred at a much faster rate than thermal decomposition at room temperature, and this will be investigated further.

Thermal transformation of pure 6-OOH **3** in CCl₄ was also followed by NMR at 70 °C. After 30 min, a new intermediate, 4-OOH **6** became evident. After 8 h, more than 70% of **3** was converted to **6**. On further heating, **6** was slowly transformed to first the allylic alcohol **7**, followed by the appearance of epoxy alcohol **8**.[12] The complete conversion of **6** to **7** and **8** (~1:3.5) took more than 60 h. In the presence of dibenzoyl peroxide, a radical initiator, the 1,3-allylic isomerization was speeded up by >5 times, supporting a possible radical mechanism.[9]

In summary, our experiments demonstrate the formation of two stable hydroperoxides in the photooxygenation of **1**. Their transformations lead to four other monooxygenated intermediates and products. We have shown that dioxetane may arise via a route other than 1,2-cycloaddition of singlet oxygen to alkene. Dioxetane is definitely the intermediate species under both thermal and acidic Hock cleavage of allylic hydroperoxide in our system. Whether this is generally true for other systems awaits further investigation. Investigation of solvent and substituent effects on product distribution and rate of reaction are under way and will be reported in due course.

Acknowledgment. We thank Kang Zhi-quan's group, Cai Mei, and Li Bao-fang for recording the MS and FT-IR spectra.

Supplementary Material Available: ¹H NMR, FT-IR, mass spectral, and GC spectral data for **1–8** (2 pages). Ordering information is given on any current masthead page.

Model Copolymerization Reactions. Direct Observation of a "Penultimate Effect" in a Model Styrene–Acrylonitrile Copolymerization

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Forty years after the publication of the classical kinetic scheme for radical copolymerization,[1,2] there is still debate concerning the factors that control composition and comonomer sequence in some copolymer chains. Interest in this problem arises not only from an intrinsic desire to understand the copolymerization process but also from the realization that alternative kinetic models of copolymerization predict very different copolymer chain structures. For example, Hill, O'Donnell, and O'Sullivan[3] have shown in their analysis of styrene–acrylonitrile copolymerization that the best terminal,[1,2] penultimate,[4] and complex-participation[5] models predict very similar copolymer *compositions* but very different comonomer *sequences*; in a copolymer prepared from an equimolar monomer mixture, the number fraction of styrene sequences which
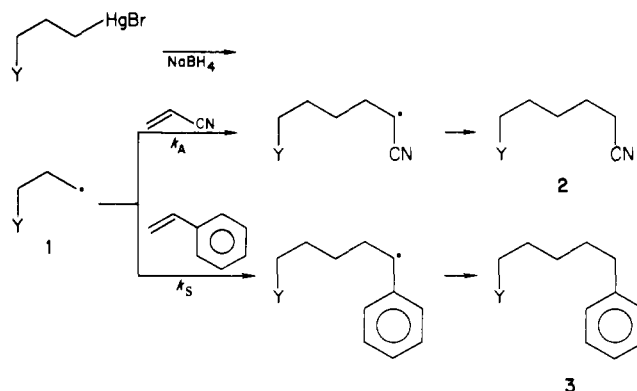
† Carnegie-Mellon University.
‡ University of Massachusetts.
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Scheme I

Table I. Relative Rates of Addition of Styrene (S) and Acrylonitrile (A) to Substituted Alkyl Radicals (**1**)

γ	k_A/k_S
–CH₃	24.5 ± 1.1[a]
–CH₂CH₂CH₃	26.2 ± 2.4
–Ph	22.6 ± 2.0
–CN	6.8 ± 0.6

[a] Rate constant ratios are reported as mean ± standard deviation for a minimum of five determinations.

consist of an isolated styrene unit is predicted to be 0.74 for the terminal model, 0.61 for the penultimate model, and 0.18 for the unrestricted complex-participation model. Clearly the synthesis of well-defined copolymer structures requires a precise understanding of copolymerization mechanism.

Hill et al. conclude on the basis of their comonomer sequence analyses that the penultimate model provides the best description of the radical copolymerization of styrene and acrylonitrile. They report $r_{SS} = 0.229$, $r_{AS} = 0.634$, $r_{AA} = 0.039$, and $r_{SA} = 0.091$; i.e., regardless of the identity of the terminal unit, the relative affinity of the growing macroradical for acrylonitrile appears to be depressed approximately 2.5-fold by a cyano group γ to the radical center. Is a substituent effect of this magnitude plausible?

In this paper we report direct measurements of the relative rates of addition of styrene and acrylonitrile to simple alkyl radicals bearing γ-phenyl and γ-cyano substituents. We believe this to be the first direct determination of the magnitude of the substituent effects which must be operative if the penultimate model is to be a physically meaningful description of radical copolymerizations of monosubstituted olefins.[6]

The radicals of interest were generated at room temperature by reduction of the corresponding alkylmercuric bromides[7] with NaBH₄ in deoxygenated DMF,[8] according to Scheme I.[9] Mass balance experiments confirmed that at least 91% of each monomer could be accounted for in terms of this reaction scheme,[10] so that the rate constant ratio k_A/k_S could be determined from measurement of the relative yields of **2** and **3** as a function of the

(6) Giese and Engelbrecht have reported very recently (Giese, B.; Engelbrecht, R. *Polym. Bull.* **1984**, *12*, 55) on the influence of β- and γ-substitution on the nucleophilicity of alkyl radicals and on the selectivity of addition of alkyl radicals to olefins. Although none of their experiments is a direct analogue of a radical copolymerization, their results and conclusions are quite consistent with our own.
(7) Each of the alkylmercuric bromides afforded C, H, N analyses that were within 0.2% of theoretical for each element.
(8) Hill and Whitesides have reported that reduction of alkylmercuric halides in O₂-saturated DMF produces alcohols and borate esters in good yields: Hill, C. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 870.
(9) A reaction sequence analogous to Scheme I has been suggested by Giese[9b] and is consistent with the mechanistic proposals of Whitesides and San Filippo.[9a] (a) Whitesides, G. M.; San Filippo, J. *J. Am. Chem. Soc.* **1970**, *92*, 6611. (b) Ito, H.; Giese, B.; Engelbrecht, R. *Macromolecules* **1984**, *17*, 2204 and references therein.
(10) Mass balance experiments were performed for *n*-butylmercuric bromide and *n*-hexylmercuric bromide, according to our standard kinetic procedure.[11] The ratio of concentrations of styrene and acrylonitrile was fixed at 3:1, as was the ratio of total monomer to organomercurial.