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 CCl_4 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** ($\sim$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 substitutent effects on product distribution and rate of reaction are under way and will be reported in due course.

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

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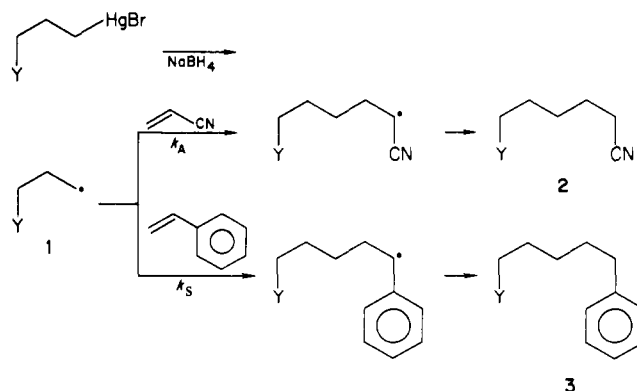
Table I. Relative Rates of Addition of Styrene (S) and Acrylonitrile (A) to Substituted Alkyl Radicals (1)

γ	k_A/k_S
$-CH_3$	24.5 ± 1.1^a
$-CH_2CH_2CH_3$	26.2 ± 2.4
$-Ph$	22.6 ± 2.0
$-CN$	6.8 ± 0.6

^{a} Rate constant ratios are reported as mean $\pm$ 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 $NaBH_4$ 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

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(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 O_2-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.

relative concentrations of the two monomers.[11,12]

The first three entries in Table I are in good agreement with rate constant ratio of 24 reported by Giese[13] for competitive addition of these monomers to cyclohexyl radical. The final two entries show that *the rate constant ratio is indeed sensitive to the nature of the γ-substituent*; 3-cyanopropyl retains a preference for addition of acrylonitrile, but this preference is reduced 3.5-fold in comparison with that shown by 3-phenylpropyl. The most likely explanation for the reduction in the relative rate of acrylonitrile addition to 3-cyanopropyl is the development in the transition state of dipolar repulsion between cyano groups on the monomer and radical. The remarkable correspondence of the γ-substituent effect measured directly in this simple model system with that calculated by application of the penultimate model to the copolymerization of styrene and acrylonitrile (vide supra) lends strong support to the use of the penultimate model as a physically meaningful description of this copolymerization.

(11) In a typical experiment, the radical precursor in deoxygenated DMF was reduced with NaBH$_4$ in the presence of precisely known, excess quantities of styrene and acrylonitrile. After 1 h at room temperature the reaction mixture was filtered (all operations in closed vessels) and the relative yields of **2** and **3** were determined by gas chromatography (for *n*-butylmercuric bromide on a 20-ft glass column, 10% Supelco SP-1000, Supelcoport support; for the other precursors on a 9-ft stainless steel column, 3% SE-30, Supelcoport support; flame ionization detection). Peak areas were determined by electronic integration (Hewlett-Packard 3380A integrator), and relative response factors were determined by injection of authentic samples of each of the monomer adducts. Identification of adducts was confirmed by combined gas chromatography–mass spectrometry, through comparison of fragmentation patterns of the nominal adducts with those of authentic samples.
(12) k_A/k_S was found to be independent of relative monomer concentrations and independent of total monomer concentration if large ($\geq$25-fold) excesses of monomer (with respect to organomercurial) were used.
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Flash Vacuum Pyrolysis of Organomanganese Pentacarbonyl Compounds

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Flash vacuum pyrolysis (fvp)[1,2] has proved to be a useful technique in both synthetic organic chemistry[3] and as a means of generating detectable concentrations of a variety of organic intermediates.[4] Considering the scale of recent interest in organometallic compounds, it is surprising that the fvp method has not been exploited for organomanganese pentacarbonyls (R–Mn(CO)$_5$), especially in view of the reactivity implied by estimates
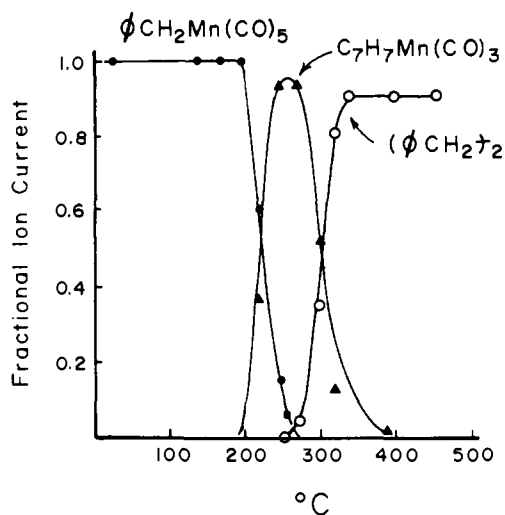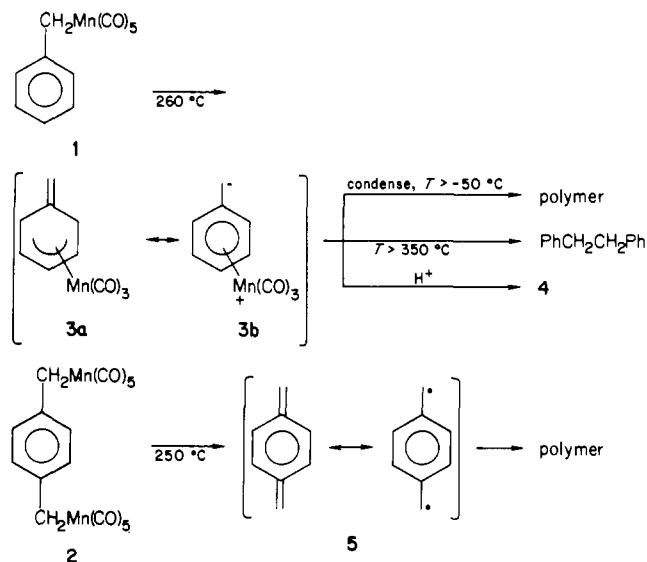
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Figure 1.

Scheme I

of the bond energies for R–Mn homolysis[5] and ligand dissociation[6] (DE $\leq$ 40 kcal/mol). We presently wish to report the results of our investigation of the reactivities of two such compounds (**1** and **2**, Scheme I) by fvp as monitored by mass spectrometry and product isolation. The results show that pentacarbonyl(phenylmethyl)manganese[7] (**1**) gives the previously unknown tricarbonyl(2-6-η^5-1-methylenecyclohexadienyl)manganese (**3**) as an intermediate which is kinetically unstable although it can be characterized at low temperature by NMR and chemical reactivity. Also, we show that the previously unknown bis(manganese) compound **2**[8] is a reasonably efficient, low temperature (260 °C) gas-phase source of *p*-xylylene (**5**).

Preliminary work showed that the benzyl compound **1** cleanly gives bibenzyl (67% yield, isolated) and metallic manganese (98% yield, titration) in our fvp system at 350 °C. Figure 1 shows the temperature profile for fvp of **1**, which was obtained at ca. 0.1

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(8) The bis(manganese) compound **2** is readily obtained from α,α'-dibromo-*p*-xylene and the sodium manganese pentacarbonyl salt in THF (68% yield, mp 140 °C dec, appropriate ^{1}H NMR, IR, mass spectral, and microanalytical results).