

to a stirred solution of KO-*t*-Bu (200 mg) in THF (10 mL) at 25 °C under N₂. After 15 min water (25 mL) was added and the reaction mixture worked up as described above to furnish **14b** (31 mg, 89%).

Reaction of 1-Phenyl-4-oxahepta-1,6-diyne (21) with Potassium *tert*-Butoxide in THF. A solution of **21** (500 mg, 2.94 mmol) in dry THF (15 mL) was added dropwise to a stirred solution of KO-*t*-Bu (500 mg, 4.5 mmol) in dry THF (20 mL) at room temperature under N₂. The mixture was stirred for 4 h. Workup provided an oil which was chromatographed on silica eluting with CH₂Cl₂/pentane (1:4) to give **22** (100 mg, 20%): mp 79–80 °C; MS *m/e* 170.0741 (C₁₂H₁₀O requires *m/e* 170.0732), 170 (M⁺, 20%), 142, 141, 139, 115 (100%), 89; ¹H NMR, see Discussion; ¹³C NMR, see Table II; IR (KBr) 1490, 1450, 1420, 1380 cm⁻¹; electronic spectrum, see Discussion. Anal. Calcd for C₁₂H₁₀O: C, 84.68; H, 5.92. Found: C, 84.57; H, 5.85.

When the reaction was carried out at 60–62 °C for 15 h, **23** (28%), mp 158–159 °C (lit.¹¹ mp 153–155 °C), identical in all observed respects to an authentic sample, was isolated.

Reaction of 22 with Potassium *tert*-Butoxide in THF. A solution of **22** (20 mg, 0.12 mmol) in THF (15 mL) was added to a stirred solution of KO-*t*-Bu (150 mg) in THF (10 mL) at 50 °C under N₂. After workup, preparative TLC on silica afforded, in addition to 4 mg of **22**, **23** (10 mg, 63%).

Reaction of 1,7-Diphenyl-4-methyl-4-azahepta-1,6-diyne (11c) with Potassium *tert*-Butoxide in THF. A solution of **11c** (1.20 g, 4.6 mmol) in THF (15 mL) was added dropwise over 2 min to a stirred solution of KO-*t*-Bu (1.0 g) in THF (10 mL) at 20 °C under N₂. After addition was complete, the mixture was stirred for a further 1 min and water (30 mL) was then added. Workup provided an oily semisolid which was recrystallized from ether as the dimer **24** (230 mg, 19.5%): mp 248–252 °C; MS *m/e* 518.2740 (C₃₈H₃₄N requires *m/e* 518.2722), 518 (M⁺, 100%), 422, 355, 257, 256; ¹H NMR (CDCl₃) δ 7.20 (m, 20 H), 5.90 (s, 4 H), 5.30 (s, 4 H), 3.35 (s, 6 H); ¹³C NMR, see Table III; IR (KBr) 3500, 3050, 2950, 1600, 1540, 1500, 1460, 1400 cm⁻¹. Anal. Calcd for C₃₈H₃₄N₂: C, 87.99; H, 6.66; N, 5.40. Found: C, 87.62; H, 6.50; N, 5.23.

The ethereal mother liquor was treated with methanol when a yellow precipitate formed which was recrystallized from

methanol to afford pale yellow crystals of **25** (190 mg, 16%): mp 209–210 °C; MS *m/e* 518 (M⁺, 92%), 422, 355, 257, 256 (100%); ¹H NMR (CDCl₃) δ 7.18 (bs, 20 H), 6.08 (s, 4 H), 4.80 (s, 4 H), 3.40 (s, 6 H); ¹³C NMR, see Table III; IR (KBr) 3500, 3050, 2950, 1600, 1540, 1500, 1460, 1400 cm⁻¹. Anal. Calcd for C₃₈H₃₄N₂: C, 87.99; H, 6.66; N, 5.40. Found: C, 87.26; H, 6.58; N, 5.29.

Reaction of 11c with Potassium *tert*-Butoxide in Benzene. A solution of **11c** (450 mg, 1.75 mmol) in benzene (25 mL) was added to a stirred solution of KO-*t*-Bu (1.0 g) in benzene (25 mL) at 20 °C under N₂. The mixture was stirred for 6 h, water (50 mL) was added, the organic layer was separated, and the aqueous layer was extracted with benzene (2 × 20 mL). The combined benzene fractions were washed with water (2 × 25 mL) and then dried (MgSO₄), and the solvent was removed under reduced pressure. The residue was chromatographed on alumina, eluting with ether/pentane (1:9), to give the following two products (in order). **18c** (55 mg, 12%, yellow oil): MS *m/e* 259.1345 (C₁₉H₁₇N requires *m/e* 259.1361), 259 (M⁺, 18%), 258, 257, 173 (100%), 172; ¹H NMR, see Discussion; IR (KBr) 3020, 2920, 1600, 1545, 1500, 1460, 1400, 1380 cm⁻¹; λ_{max} (EtOH) 263 (ε 2850), 272 (1970), 348 nm (1120). **14c** (110 mg, 24%): mp 141–142 °C (lit.⁹ mp 141–143 °C); identical in all observed respects to an authentic sample.

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Registry No. 2a, 13702-09-5; **2a** trimer, 70446-04-7; **2b**, 6921-27-3; **2c**, 13002-92-1; **5a**, 56146-99-7; **5b**, 56147-00-3; **5c**, 70445-95-3; **6a**, 56147-05-8; **6b**, 56147-06-9; **6c**, 56147-07-0; **7a**, 70445-96-4; **7b**, 70445-97-5; **7c**, 70445-98-6; **8**, 70445-99-7; **9**, 70446-00-3; **10d**, 70492-70-5; **11a**, 13225-60-0; **11b**, 13225-61-1; **11c**, 2568-62-9; **14a**, 14208-74-3; **14b**, 13225-65-5; **14c**, 13225-64-4; **18a**, 56146-95-3; **18b**, 56146-96-4; **18c**, 70446-01-4; **20**, 70446-02-5; **21**, 53877-63-7; **22**, 56146-97-5; **23**, 7193-16-0; **26**, 56146-98-6; 1-bromo-4,4-dimethylpent-2-yne, 52323-99-6; 4,4-dimethylpent-2-yn-1-ol, 52323-98-5; 3,3-dimethylbut-1-yne, 917-92-0; *N,N*-bis(butoxymethyl)methylamine, 70446-03-6.

Nucleophilic Character of Alkyl Radicals. 18.¹ Absolute Rate Constants for the Addition of Primary Alkyl Radicals to Conjugated Olefins and 1,4-Benzoquinone

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The rate constants for the addition of the 5-hexenyl radical to styrene, α -methylstyrene, butadiene, acrylic monomers, methyl vinyl ketone, and 1,4-benzoquinone were measured from 16 to 69 °C. The importance of polar effects, due to the nucleophilic character of the alkyl radical in olefin addition, is emphasized. The inhibition of chain processes by quinone is discussed in terms of the high rate constant (2.0×10^7 L mol⁻¹ s⁻¹ at 69 °C) of the alkyl radical addition to 1,4-benzoquinone.

The concept of polar effects in free-radical reactions shows ambiguous points being derived from the ionic reactions. Ionic electrophilic and nucleophilic species are formally well defined, but the electrophilic or nucleophilic character of free radicals cannot always be deduced from their formal structures, not even for radical ions (i.e., the

radical anion SO₄⁻ has a clear-cut electrophilic character) or for borderline cases such as carbon-centered free radicals. The phenomenon is kinetic in nature and the terms of electrophilicity and nucleophilicity cannot be mechanically transferred from ionic to radical reactions. For a given reaction the rate constant sequence cannot measure the relative electrophilicity and nucleophilicity of free radicals, as it occurs for ionic reactions. Moreover, fixing an electrophilic or nucleophilic character for a given

(1) Part 17: A. Citterio, F. Minisci, A. Arnoldi, R. Pagano, A. Parravicini, and O. Porta, *J. Chem. Soc., Perkin Trans. 2*, 519 (1978).

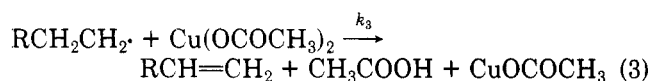
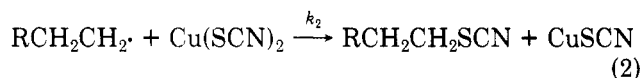
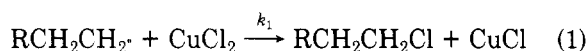
radical, without taking into account the particular reaction involved, is not strictly correct. Both the extent and the nature of the polar effect in free-radical reactions depend on the features of the radical, the substrate, and the reaction medium.

Thus it is not surprising that the simplest alkyl radical, methyl, has been considered from time to time to be slightly electrophilic,² nonpolar,³ and slightly⁴ or cleanly^{5,6} nucleophilic in atom transfer,^{2,6} in addition reactions with olefins^{4,5} and in homolytic aromatic substitution.^{3,5}

There is much more agreement about the nucleophilic character of primary alkyl radicals in their main reactions. Thus, positive ρ values were reported⁷ for hydrogen abstraction from substituted toluenes, and a clear-cut nucleophilic character has been drawn from positional and substrate selectivity in the homolytic alkylation of protonated heteroaromatic bases⁸ and in addition reactions with olefins.^{1,5b,9}

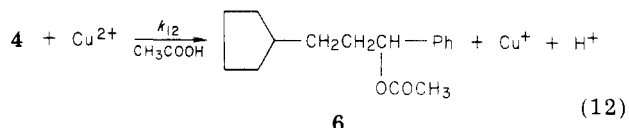
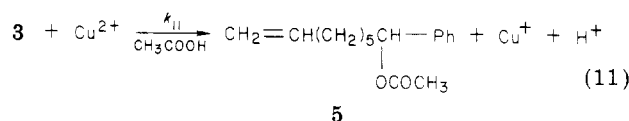
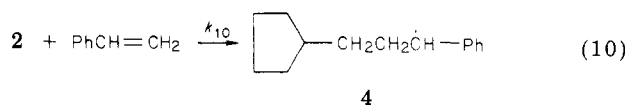
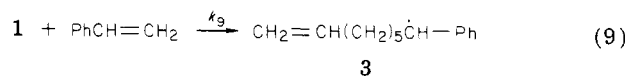
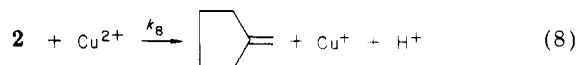
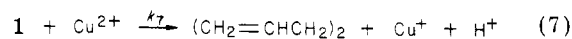
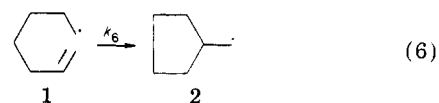
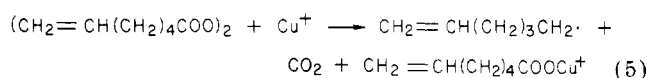
The knowledge of the absolute rate constants in the addition of alkyl radicals to industrial monomers such as styrene, butadiene, acrylic monomers, methyl vinyl ketone, and 1,4-benzoquinone involves polar effects, the structure-reactivity relationship, synthetic possibilities from cheap materials, and the inhibition of chain processes. The largest body of data on rate constants concerning carbon-centered free-radical addition to olefins has been supplied by gas-phase studies¹⁰ or by free-radical polymerization;¹¹ only a few data are available for addition rates in solution,¹⁰ which does not involve polymerization.

Previous attempts^{1,9} to determine the absolute rate constants for the addition of alkyl radicals to styrene and acrylic monomers were based on competitive methods in which the known reference constants (k_1 , k_2 , k_3) were the oxidation rates of alkyl radicals either by ligand-transfer⁹ (reactions 1 and 2) or by electron-transfer¹ (reaction 3) processes.

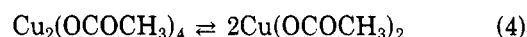


These methods, however, have some limitations since reactions 1–3 are influenced by the reaction medium. Cupric halides are generally a composite of individual species¹² (CuCl^+ , CuCl_2 , CuCl_3^- , CuCl_4^{2-}), which can all

Scheme I



transfer a chlorine atom, according to reaction 1, very probably with different rates; the ratios among these individual species are considerably affected by the salt concentration, the nature of the solvent, and the reagents. Due to the very high values of k_1 and k_2 , reactions 1 and 2 are suitable for kinetic studies only with very reactive substrates. Also the rate of reaction 3 is influenced by the medium, as it strictly depends on the monomer-dimer equilibrium¹³ (eq 4).



To avoid these complications, we have chosen a kinetic model based on the irreversible isomerization of the 5-hexenyl radical to the cyclopentylmethyl radical, a process which is quite independent of the solvent. This model is suitable for determining absolute rate constants in the range 10^4 – 10^7 L mol⁻¹ s⁻¹ for reactions involving primary alkyl radicals, by product analysis.⁸

Results

The main problem in determining rate constants in the addition of alkyl radicals to butadiene, styrene, and acrylic monomers consists in cleanly avoiding polymerization or telomerization of the monomers. Such a problem does not exist with 1,4-benzoquinone which has no tendency to polymerize and, on the contrary, is a polymerization inhibitor. In order to reach this result, we found it necessary to use two different kinetic models, both based on the copper(I)-catalyzed decomposition of di-6-heptenoyl peroxide as the free-radical source.

Kinetic Model I. The alkyl radical addition to an olefin involves the steps of Scheme I (eq 5–12, exemplified for styrene), with $k_6 = 10^{10.7}e^{-7.8/\theta}$ L mol⁻¹ s⁻¹ taken from literature.¹⁴ Since allylic and benzylic radicals are efficiently oxidized by cupric acetate also in the presence of

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Table I. Rate Constants ($\text{L mol}^{-1} \text{s}^{-1}$) for the Addition of the 5-Hexenyl Radical to Some Conjugated Olefins at 25 and 69 °C and Relative Arrhenius Parameters

substrate	rate at 25 °C ^a		rate at 69 °C ^a		Arrhenius parameters ^a	
	absolute	relative	absolute	relative	$E_a \pm 0.4$, kcal/mol	$\log A \pm 0.5^b$
α -methylstyrene			8.9×10^4	0.60		
styrene	5.4×10^4	1	1.5×10^5	1	4.88	8.33
butadiene	9.2×10^4	1.71				
methyl acrylate	2.1×10^5	3.59	5.2×10^5	3.47	3.72	8.22
α -methacrylic acid			6.6×10^5	4.40		
acrylic acid	3.6×10^5	6.78	7.0×10^5	4.67	3.22	8.00
methyl vinyl ketone			8.7×10^5	5.80		
acrylonitrile	5.28×10^5	9.77	11.3×10^5	7.53	3.29	8.30
benzoquinone			2.0×10^7	133		

^a Deduced assuming k_6 from ref 14; $k_6 = 9.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C and $k_6 = 5.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 69 °C. ^b Standard deviation from experimental data.

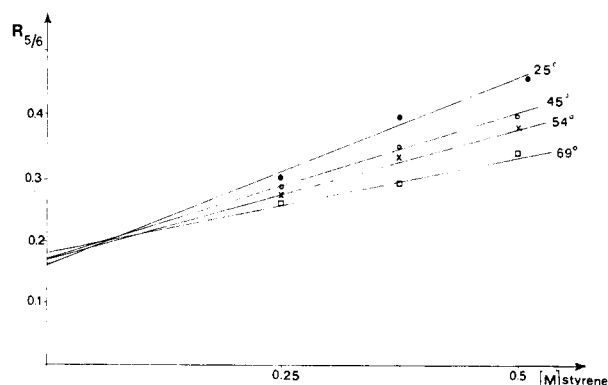
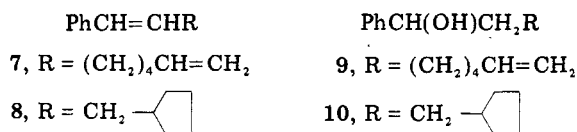


Figure 1. Dependence of the ratio (R) of the addition products on styrene concentration at different temperatures.

the monomer excess, this scheme was used for styrene, α -methylstyrene, and butadiene. A similar one was used with 1,4-benzoquinone, for which the oxidation reaction gives only substitution products. No traces of dimerization, telomerization, or polymerization coming from the benzylic radicals **3** and **4** occur under the reaction conditions. Small amounts (5%) of the olefins **7** and **8** and the alcohols **9** and **10** are directly formed from oxidation of the radicals **3** and



4 by cupric acetate or during the isolation and the analysis of the esters **5** and **6**; their presence, however, does not affect the validity of kinetic scheme. The steady-state assumption for radicals **1** and **2** allows derivation of kinetic eq 13 (Appendix A) from eq 5–12 of Scheme I; if we assume

$$[5]/[6] = k_9[\text{PhCH=CH}_2]/k_6 + k_8[\text{Cu}^{2+}]/k_6 \quad (13)$$

that $k_9 \approx k_{10}$, the addition is irreversible, and the $[\text{Cu}^{2+}]/[\text{Cu}^+]$ ratio is constant on the basis of previous works.¹⁵

At low conversions, the products ratio $[5]/[6]$ is linearly correlated with the initial styrene concentration (Figure 1) in the temperature range 25–69 °C, at constant cupric salt concentration (0.025 M). A least-squares treatment allows evaluation of k_9/k_6 from the slope and k_8/k_6 from the intercept. The rate constant k_9 at 25 and 69 °C and the Arrhenius parameters for the addition reaction are reported in Table I. The value of $k_8 = (6.5 \pm 0.7) \times 10^5$

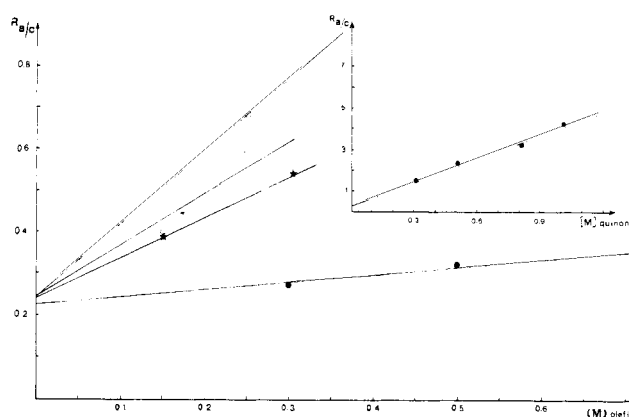
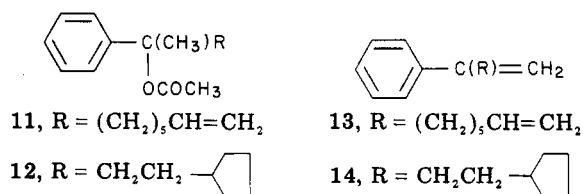


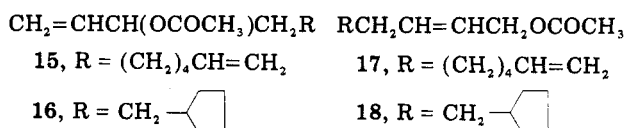
Figure 2. Dependence of the ratio (R) of the addition products **a** and **c** for methyl vinyl ketone (\square), methacrylic acid (\circ), butadiene (\star), α -methylstyrene (\bullet), and quinone on olefin concentration (all reactions at 69 °C, except butadiene reaction at 25 °C).

$\text{L mol}^{-1} \text{ s}^{-1}$ at 25 °C, estimated for all the cupric salt without considering the monomer–dimer equilibrium (eq 4), is slightly lower than the reported one¹³ ($1.2 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ at 25 °C).

The behavior of α -methylstyrene is strictly analogous. The dependence of the pyrolysis products **13** and **14** (arising from the acetates **11** and **12**) on the α -methyl-



styrene concentration is shown in Figure 2. An equation analogous to eq 13 allows evaluation of the addition rate constant $k = (8.9 \pm 1.1) \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ at 69 °C. With butadiene both 1,2 and 1,4 isomer esters **15**, **16**, **17**, and **18** are formed. Examination of the data in Figure 2 for

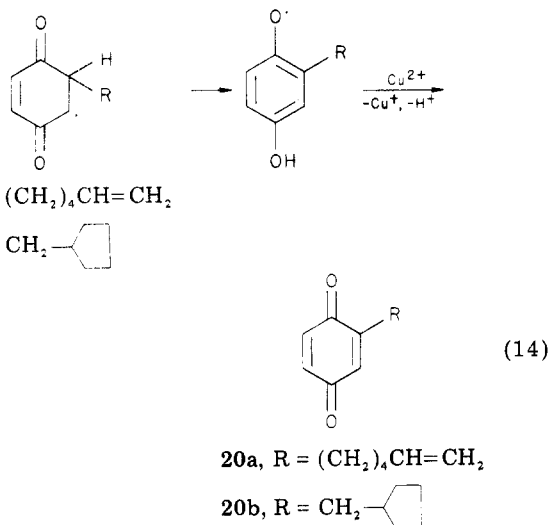


the ratio $([15] + [17])/([16] + [18])$ against butadiene concentration gives a rate constant of $(9.2 \pm 0.2) \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ at 25 °C.

Somewhat different is the behavior of 1,4-benzoquinone because the oxidation of the intermediate radicals **19a** and **19b** by cupric salts leads to the alkylquinones **20a** and **20b**

(15) J. K. Kochi and A. Benis, *J. Am. Chem. Soc.*, **90**, 4038 (1968).

(eq 14). Whether the cupric ion oxidizes the radicals **19a**



and **19b** or the corresponding enols depends on the relative rates of oxidation or enolization. However, this is irrelevant for kinetic purposes, because a very effective redox chain also takes place in this case. From the data of the ratio **[20a]/[20b]** (Figure 2) against quinone concentration, a rate constant of $(2.0 \pm 1) \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ at 69 °C can be obtained. The high reactivity of benzoquinone determines a high yield of **20a**, so the ratio **[20a]/[20b]** is not very sensitive to quinone concentration and the accuracy of the analytical results is somewhat affected.

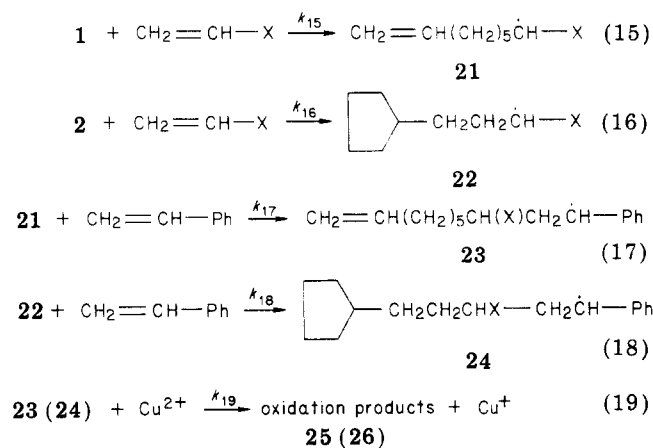
Kinetic Model II. The previous model is not suitable for acrylic monomers and methyl vinyl ketone, because cupric acetate does not prevent these olefins from polymerizing.¹⁶ We have used a somewhat more complex kinetic model, related to Scheme I and based on the alternating addition of primary alkyl radicals to a couple of olefins.¹ One of these is always styrene, whereas the other is the acrylic monomer or methyl vinyl ketone. In addition to reactions 5–12 of Scheme I, radicals **1** and **2** undergo the addition reactions (15) and (16) of Scheme II.

The basis of the scheme is the fact that k_{17} and k_{18} are higher than the propagation rates of homopolymerization ($10\text{--}10^3 \text{ L mol}^{-1} \text{ s}^{-1}$)¹¹ of these monomers, due to the electrophilic character of the radicals involved. For this reason the addition to styrene is the only reaction of radicals **21** and **22** in proper range of monomer concentrations. This is the key step of the alternating effect in free-radical copolymerization. No oxidation of the radicals **21** and **22** occurs, always due to their electrophilic character.¹⁷

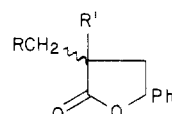
The oxidation products **25** and **26** are the lactones **25a** and **26a** for acrylic acid, **25b** and **26b** for methacrylic acid, the cyano esters **25c** and **26c** for acrylonitrile, a mixture of **25a** and **26a** and the acetic esters **25d** and **26d** for methyl acrylate, and the γ -hydroxy ketones **25e** and **26e** for methyl vinyl ketone. In all cases compounds **5** and **6** were side reaction products.

The steady-state assumption for the radicals involved in Schemes I and II leads to kinetic eq 20–22 (Appendix B), assuming $k_9 \approx k_{10}$, $k_{15} \approx k_{16}$, and $k_7 \approx k_8$.

Scheme II



X = CN, COOMe, COOH, COMe



25a, R = (CH₂)₄CH=CH₂, R' = H

26a, R = CH₂-, R' = H

25b, R = (CH₂)₄CH=CH₂, R' = CH₃

26b, R = CH₂-, R' = CH₃

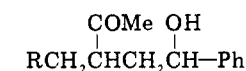


25c, R = (CH₂)₄CH=CH₂, X = CN

26c, R = CH₂-, X = CN

25d, R = (CH₂)₄CH=CH₂, X = COOCH₃

26d, R = CH₂-, X = COOCH₃



25e, R = (CH₂)₄CH=CH₂

26e, R = CH₂-

$$\frac{[25]}{[26]} = \frac{k_{15}}{k_6} [\text{CH}_2=\text{CHX}] + \frac{k_{10}}{k_6} [\text{CH}_2=\text{CHPh}] + \frac{k_8}{k_6} [\text{Cu}^{2+}] \quad (20)$$

$$\frac{[5]}{[6]} = \frac{k_{16}}{k_6} [\text{CH}_2=\text{CHX}] + \frac{k_9}{k_6} [\text{CH}_2=\text{CHPh}] + \frac{k_8}{k_6} [\text{Cu}^{2+}] \quad (21)$$

$$\frac{[25]}{[5]} = \frac{[26]}{[6]} = \frac{k_{16}}{k_{10}} \frac{[\text{CH}_2=\text{CHX}]}{[\text{CH}_2=\text{CHPh}]} \quad (22)$$

Analysis of the ratio of the oxidation products **25** and **26** (or **5** and **6**) against the acrylic monomer concentration in all cases shows the linearity foreseen from eq 20 and 21 (Figures 3–5). The intercepts have very similar values (the median value was 0.22) for all substrates, at a constant concentration of cupric acetate (0.025 M) and styrene (0.25 M); the value of $k_8 = (9 \pm 1) \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$ at 25 °C estimated at constant cupric salt concentration agrees with the reported value¹³ ($1.2 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ at 25 °C). The slopes differ and allow evaluation of the addition constants

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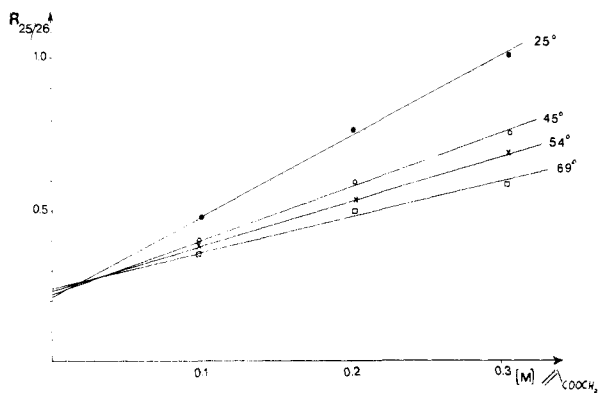


Figure 3. Dependence of the ratio (R) of the addition products **25a** and **26a** on methyl acrylate concentration at different temperatures.

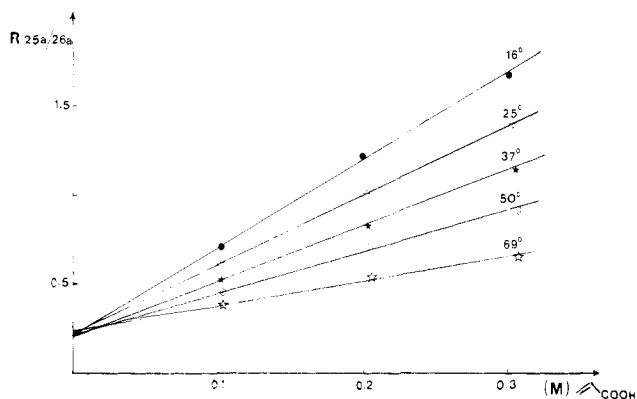


Figure 4. Dependence of the ratio (R) of the addition products **25a** and **26a** on acrylic acid concentration at different temperatures.

k_{15} of the 5-hexenyl radical to acrylic and methacrylic acids, acrylonitrile, and methyl vinyl ketone. Internal consistency of the data was checked by eq 22. The results are summarized in Table I at 25 and 69 °C with the Arrhenius parameters deduced for acrylic acid, methyl acrylate, and acrylonitrile (Figure 6). These values differ somewhat in some cases from the ones previously reported¹ and, in our opinion, are more exact because the kinetic model has less experimental error.

Compounds **25e** and **26e**, arising from methyl vinyl ketone, do not originate from the hydrolysis of the corresponding acetates because it has been verified that no substantial hydrolysis takes place under the reaction conditions. The mechanism of Scheme III could explain such a result.

The intramolecular addition of an alkyl radical to a keto group appears to be a very fast reaction as it competes with the fast hydrogen abstraction from the trialkyltin hydride radical ($k = 1 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ at 25 °C).¹⁸ This result seems to disagree with other ones of similar radicals, for which no intramolecular addition to the carbonyl group was taken in account;¹⁹ however, in this case a detailed study of the mechanism excluding an intramolecular addition to the carbonyl group was not carried out. An analogous mechanism could explain the formation of lactones **25a** and **26a** with methyl acrylate (in addition to the acetates **25d** and **26d**): a competition between the oxidation of the benzyl radical with formation of the acetates and intramolecular addition to the ester group

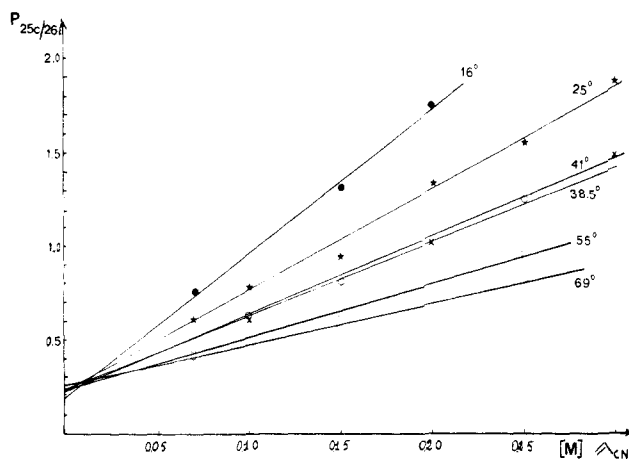


Figure 5. Dependence of the ratio (R) of the addition products **25c** and **26c** on acrylonitrile concentration at different temperatures.

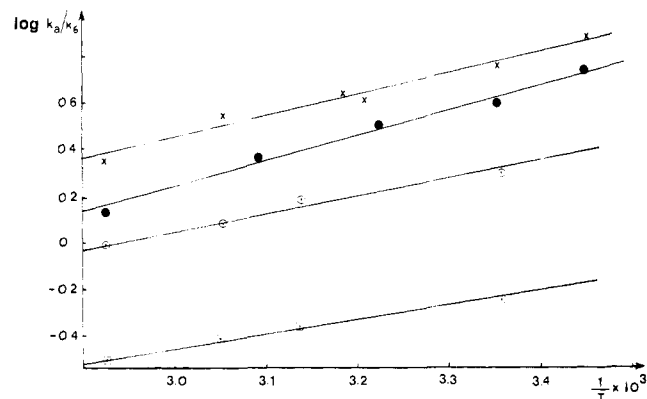
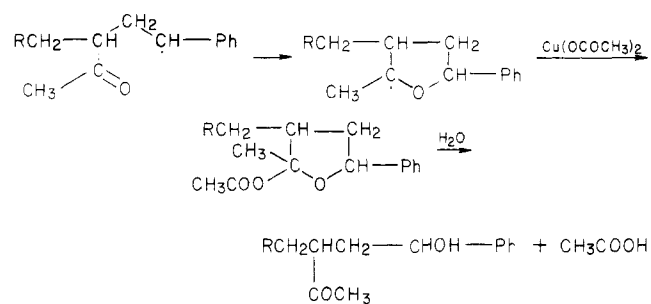
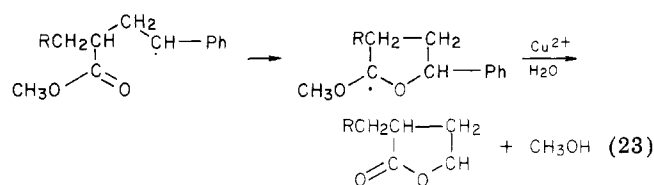


Figure 6. Arrhenius plot of k_a/k_6 for the substrates acrylonitrile (\times), acrylic acid (\bullet), methyl acrylate (\circ), and styrene (\square) in the addition of the 6-hexenyl radical.

Scheme III



with formation of lactones (eq 23) could cause this behavior.



With acrylic and methacrylic acids a similar radical mechanism or an ionic one, involving the benzylic radical oxidation, could well explain the lactone formation. Intramolecular addition of alkyl radicals to carbonyl groups of esters²⁰ and acids²¹ has been reported.

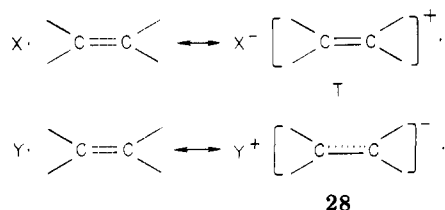
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Discussion

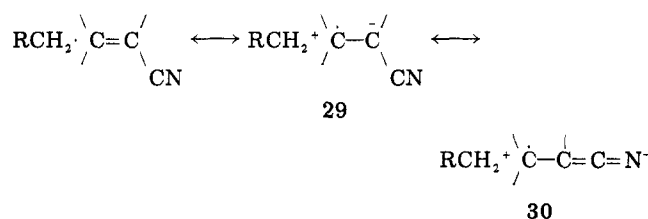
Long ago²² Walling suggested that polar structures such as 27 and 28 could contribute to the transition state of radical addition reactions (respectively with electrophilic and nucleophilic species).



In terms of frontier orbital theory this picture could reflect a favorable SOMO/LUMO interaction in addition of alkyl radical to electron-deficient olefins, keeping in mind that the theory applies to the early stages of the interaction between orbitals, but it is not really about the transition state itself. Recent ab initio molecular orbital studies²³ further suggest that the radical additions are dominated mainly by the charge-transfer (CT) interaction. Moreover, the importance of charge-transfer structures in free-radical addition to olefins has also recently been emphasized in the addition of carbon-centered radicals to olefins.²⁴

As a satisfactory quantitative theoretical approach is at present lacking, this qualitative picture is still valid in explaining our results obtained with primary alkyl radicals.

A transition state similar to a charge-transfer complex (structures 29 and 30) determines a large contribution of



the polar effect to the activation energy, whereas in a transition state similar to the intermediate radical CH_2CHCN , the rate is mainly determined by the reaction enthalpy. The partition of activation energy between enthalpy, related to the starting olefin and intermediate radical stability, and polar contribution is quite a hard problem.²⁵ However, it is reasonable to assume that in the absence of steric hindrance (as indicated by the similarity of preexponential factors in Table I) polar effects determine a smaller activation energy in acrylic monomers with respect to styrene, as the resonance energy is certainly higher for benzyl radicals than for the corresponding radicals arising from acrylic monomers.

The results of Table I clearly indicate that the nucleophilic character of the 5-hexenyl radical plays a significant role in determining the sequence of the addition rates. The linear correlation of the rates at 69 °C against σ_p^- and σ_p of the olefin substituent ($\rho = 1.19$ and $\rho = 1.15$, respectively, Figure 7) indicates that structures like 29 and 30 would contribute to the observed sequence. The σ_p^-

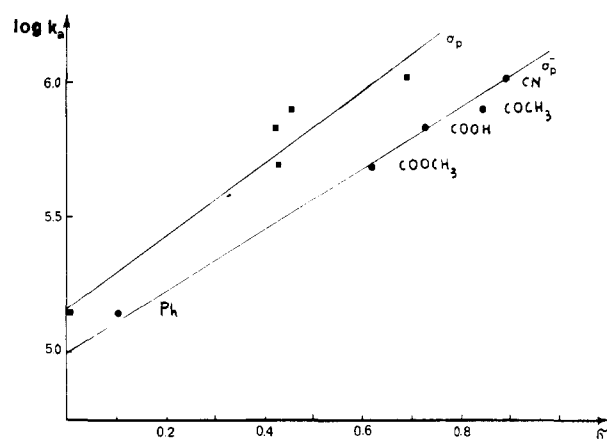


Figure 7. Hammett plot against σ_p^- for the rate constants of the addition of the 6-hexenyl radical to some conjugated olefins.

constants give better correlation ($r = 0.997$) than σ_p ($r = 0.994$), but the difference is not very significant, even if σ_p^- gives the correct sequence for COCH_3 and COOCH_3 .

Two facts concerning the polar effects need consideration. The relatively high free-radical reactivity of styrene and butadiene (compared to that of ethylene) has always been ascribed to the stability of the intermediate benzyl and allyl radicals. However, the deviation of styrene from linearity in the correlation of Figure 7 is relatively small (as indicated by correlation coefficient); this could be the fortuitous result of a balance between the higher stability of the benzyl radical and the lower polar effect of phenyl which is an activating conjugative group for both electrophilic and nucleophilic species (as is shown by σ_p^+ and σ_p^- values²⁶) and a slightly electron-withdrawing inductive group. However, the polar effect could dominate the reactivity sequence also with styrene, especially if we consider a transition-state structure different from the intermediate radical adduct. The results obtained with α -methylstyrene and methacrylic acid are particularly significant as concerns the role of the polar effects: both are somewhat less reactive than styrene and acrylic acid, respectively. Thus the deactivating polar effect of a poor electron-releasing group, such as methyl, overcomes the expected activating effect determined by the formation of a tertiary alkyl radical. A similar deactivating effect, deduced by relative rates, of the methyl group was already reported^{27,5b} and recently confirmed.²⁸ In contrast, the methyl radical has been reported to be more reactive²⁹ with acrylic acid and styrene than with methacrylic acid and α -methylstyrene. With 1,4-benzoquinone the intermediate radical stabilization and polar effects act in the same direction. However, it is surprising how rate constants for the addition of free radicals to quinones are presently lacking, if we consider the well-known importance of quinones as free-radical scavengers and as chain-process inhibitors. The high rate constant now determined with primary alkyl radicals enables us to better understand the quinones effectiveness in trapping free radicals. The importance of polar effects in determining this high rate is also shown by the low reactivity of electrophilic radicals such as amino radicals protonated or coordinated with metal salts, which do not react at all with *p*-benzo-

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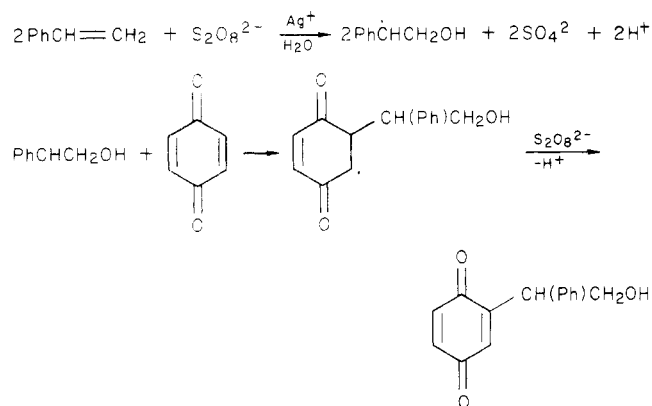
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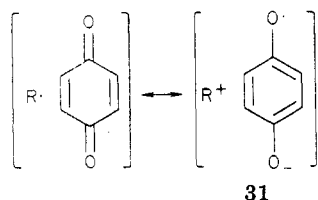
Scheme IV



quinone,³⁰ or oxygen-centered radicals, which react faster with olefins,³¹ with aromatics,³¹ and in hydrogen abstraction.³² On the other hand, the effectiveness as a polymerization inhibitor is much higher for styrene and vinyl acetate,³³ which originate nucleophilic carbon-centered radicals, than for acrylates, in which the electron-withdrawing group increases the electron affinity of the corresponding radical. This behavior has been recently confirmed^{31a} in the styrene oxidation by silver-catalyzed decomposition of peroxydisulfate in the presence of *p*-benzoquinone. No polymerization and telomerization of styrene was observed, but the benzyl radical was completely scavenged by benzoquinone, and 2-(2-hydroxy-1-phenylethyl)-1,4-benzoquinone was obtained (Scheme IV).

The high rate of quinone reaction toward nucleophilic radicals also suggests the possibility of the quinone-hydroquinone system synergism in inhibiting chain reactions such as autoxidation involving alkyl and peroxy radicals: quinone reacts faster with nucleophilic alkyl radicals and hydroquinone reacts faster with electrophilic peroxy radicals, both yielding similar stabilized radicals, which are too unreactive to carry on the chain.

Contribution to the transition state of polar form 31 can



explain these results. The degree of charge separation depends on donor character of the radical and the acceptance character of the quinone, a complete electron transfer being the limit case. This latter could explain the variable preference of free-radical attack at a carbon or oxygen atom of the quinone. Thus quinones with high potentials, such as chloranil, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and quinizarinquinone react with nucleophilic radicals such as acyl³⁴ and allyl^{31b} radicals at the oxygen atom, whereas 1,4-benzoquinone and alkyl-quinones are attacked by the same radicals at the carbon atom^{31a,35} and 2,3,5,6-tetramethyl-1,4-benzoquinone does

(30) Unpublished results of this laboratory.

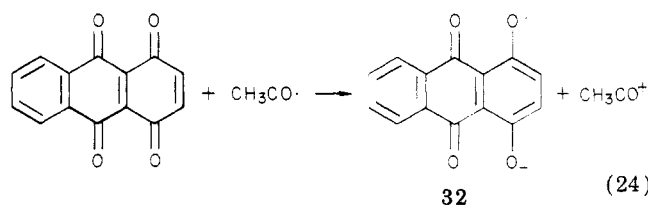
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not react with acyl radicals.³⁵ An electron-transfer process should explain the attack at the oxygen atom (eq 24).



Depending on the reaction medium, the relatively stable and persistent radical anion 32 can either react with acyl cations or scavenge an acyl radical giving in the case of quinizarinquinone the corresponding monoacetate.

Summary

The positive ρ value observed for the addition of the 5-hexenyl radical to substituted olefins clearly indicates the nucleophilic character of a primary alkyl radical in an olefin addition. The stabilization of the transition state by polar structures $\text{R}^+\cdot\text{CH}_2\text{-CHX}$ explains the activation energies order reversed from that predicted by the resonance stabilization effect in substituted olefins, and it is the main factor in determining the high trapping effectiveness of 1,4-benzoquinone. Complete electron transfer from radical to substrate is a limit case, which could explain the different reaction course observed with quinones of high electron affinity and radicals with low ionization potential.

The knowledge of the rate constants of alkyl radical additions to olefins, together with their oxidation rates, has also interesting synthetic potential for allowing selection of the best conditions for the synthesis of a variety of polyfunctional products starting from cheap industrial monomers.

Experimental Section

Melting and boiling points are uncorrected. NMR spectra were run in CDCl_3 (Me_4Si as internal standard), using a Varian A 90 (or A 100) spectrometer. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6D mass spectrometer at 70 eV, using an all-glass inlet system operating at 200 °C. IR spectra were obtained on a Perkin-Elmer E-177 grating infrared spectrometer.

Gas chromatographic (GC) analyses were performed on a Hewlett-Packard 5850 or a DANI 3600 chromatograph, using an 8 ft \times 1/8 in. 10% UCC on Chromosorb W AW-DMCS column and an 8 ft \times 1/8 in. 3% OV₁₇ on Chromosorb P 60-80 mesh column. Preparative-scale GC analyses were performed on a Varian Aerograph Model 90-P with a thermal conductivity detector. The columns used were as follows: 10 ft \times 1/4 in. OV₁₇ 20% on Chromosorb W and 10 ft \times 1/4 in. 20% UCC on Chromosorb W (60-80 mesh).

All reactions were run in a constant-temperature bath controlled with ± 0.1 °C.

Materials. Acetic acid and acetonitrile were refluxed and distilled over P_2O_5 under N_2 . Styrene, α -methylstyrene, acrylonitrile, acrylic and methacrylic acids, and methyl vinyl ketone were redistilled under N_2 at 100 mmHg immediately before use. 1,4-Benzoquinone was purified by sublimation (mp 115-116 °C). Butadiene was distilled by the trap-to-trap method. Hexadiene and methylenecyclopentane were commercial products. Di-6-heptenoyl peroxide was prepared as described previously³⁶ from 6-heptenoyl chloride (bp 35 °C (1 mmHg)), H_2O_2 , and pyridine;³⁷ the residual solvents were removed at 0 °C under vacuum for 6 h, and the peroxide was stored at -30 °C (its purity by iodometric

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Table II. Rate Constants (k_a (L mol⁻¹ s⁻¹)) and Correlation Coefficients (r) for the Addition of the 5-Hexenyl Radical to Conjugated Olefins^a

olefin	t , °C	k_a	r
α -methylstyrene	69	8.9×10^4	0.9962
styrene	69	1.5×10^5	0.9987
styrene	54	1.2×10^5	0.9937
styrene	45	9.4×10^4	0.9988
styrene	25	5.4×10^4	0.9998
butadiene	25	9.2×10^4	0.9981
methyl acrylate	69	5.9×10^5	0.9998
methyl acrylate	54	4.5×10^5	0.9987
methyl acrylate	45	3.8×10^5	0.9939
methyl acrylate	25	2.6×10^5	0.9981
α -methacrylic acid	69	6.6×10^5	0.9866
acrylic acid	69	7.1×10^5	0.9928
acrylic acid	50	6.0×10^5	0.9967
acrylic acid	37	4.9×10^5	0.9988
acrylic acid	25	3.8×10^5	0.9978
acrylic acid	16	2.4×10^5	0.9900
methyl vinyl ketone	69	8.7×10^5	0.9977
acrylonitrile	69	11.3×10^5	0.9996
acrylonitrile	55	8.7×10^5	0.9893
acrylonitrile	41	7.6×10^5	0.9993
acrylonitrile	38.5	6.6×10^5	0.9950
acrylonitrile	25	5.3×10^5	0.9937
acrylonitrile	16	4.7×10^5	0.9996
<i>p</i> -benzoquinone	69	2.0×10^7	0.9883

^a All of the data summarized in this table are available for the interested reader.

analysis was 98%). The same procedure was used with 2-cyclopentaneacetic acid (bp 125 °C (25 mmHg)) to obtain dicyclopentyl acetyl peroxide. The stock solution of copper(I) acetate was prepared as an acetonitrile complex by stirring 1.45 g (8×10^{-3} mol) of Cu(OCOCH₃)₂ with an excess of copper powder in 100 mL of a degassed CH₃CN-CH₃COOH (4:6) mixture under N₂. The solution was standardized against 0.1 N Ce(SO₄)₂.

The standard solutions for the study of the addition reactions were prepared by dissolving under N₂ weighed amounts of Cu(OCOCH₃)₂ (0.025 M), vinylic monomer (0.03–0.7 M), and 1 mL of a stock solution of copper(I) acetate in a degassed mixture of CH₃CN-CH₃COOH (6:4) into 100 mL.

Kinetic Procedure and Analysis. Stock reagent solutions (25 mL) were poured into a degassed 50-mL flask and thermostated for 30 min under N₂ at the selected temperature. To the magnetically stirred solution di-6-heptenoyl peroxide (6.0×10^{-3} g) was added and the reaction run for 2 h under N₂. All reactions were carried out in duplicate and in a few cases were repeated four or five times.

The solution was poured into ethyl ether (40 mL), water (30 mL) was added, and the organic layer was separated. The water solution was extracted twice with ether (two 30-mL portions), and the combined organic extracts were washed with water (four 30-mL portions) and dried on Na₂SO₄. The product distribution resulting from the various reactions was analyzed by GC. Calibration curves for concentration vs. peak area were prepared for the reaction products by using standard solutions of mixtures of authentic samples in toluene. The material balance was always good; 90–100% of the theoretical products from the heptenoyl peroxide are accounted for and include hexadiene, methylene-cyclopentane, and the addition products. The results are summarized in Table II and, graphically, in Figures 1–5. Heptenoic acid was quantitatively determined by using an 8 ft \times 1/8 in. 10% FFAP on Chromosorb P 60-80 mesh column; its yield was 90–95% on peroxide. The values of k_a/k_6 and k_8/k_6 were calculated for each insaturated compound by using linear regression analysis. The errors quoted represent 95% confidence limits on each slope and intercept.

Product Identification. All cyclized addition products were prepared as pure samples by the following procedure: dicyclopentyl acetyl peroxide (1.5 g, 5.1×10^{-3} mol) was added under N₂ in 1 h to 50 mL of a solution of styrene (0.4 M) [or α -methylstyrene (0.5 M), butadiene (0.3 M), or styrene (0.25 M) and vinyl monomer (0.3 M)] in CH₃CN-CH₃COOH (6:4) containing CuOCOCH₃ (0.005 M) and Cu(OCOCH₃)₂ (0.025 M) at

40 °C. The reaction mixture was concentrated to 20 mL on a rotary evaporator, ethyl ether (100 mL) and water (100 mL) were added, the layers were separated, and the aqueous portion was extracted twice with pentane (two 50-mL portions). The combined extracts were washed with water (three 50-mL portions), dried on Na₂SO₄, and evaporated. The residue was chromatographed on silica gel eluting with hexane-ethyl acetate (9:1) to give the addition products in yields ranging from 55% (for α -methylstyrene) to 80% (for acrylic acid and methyl vinyl ketone). The isolated products were found to be identical with those isolated by preparative GC from the kinetic runs.

The addition products to 1,4-benzoquinone **20b** (2-cyclopentylmethyl-1,4-benzoquinone) were synthesized following the reported procedure³² based on the Ag⁺-catalyzed oxidation of cyclopentaneacetic acid by peroxydisulfate in the presence of quinone (82% yield). Analytical data for **20a** and **20b** are reported elsewhere.^{31a}

Compounds **11** and **12** were identified as a mixture by NMR spectra because TLC separation was impossible. The quantitative response of the signals at δ 7.3 (s, aromatics), 4.9–5.8 (m, terminal vinyl), and 2.2 (s, OCOCH₃) was checked for analysis, but the intrinsic error of the method precluded its use. The analyses of these compounds were carried out on the pyrolysis products **13** and **14**, obtained by introducing the kinetic runs in the gas chromatograph at 280 °C injection temperature.

All the other reaction products were isolated from kinetic runs by preparative vapor-phase chromatography, and elemental analyses agree well in all cases.

1-Phenyl-7-octen-1-yl Acetate (5): IR ν_{\max} 1740 (CO), 1645 (CH=CH₂), 910 cm⁻¹; NMR (CDCl₃) δ 7.3 (s, Ar, 5 H), 5.75 (t, CHOAc, 1 H), 4.8–6.0 (m, vinyl, 3 H), 2.05 (s, COCH₃, 3 H), 2.2 (dt, CH₂CH=CH₂, 2 H), 1.2–1.8 (m, 8 H); MS m/e 246 (M⁺), 204, 186, 149, 117, 104, 91, 77.

3-Cyclopentyl-1-phenylpropan-1-yl Acetate (6): bp 75 °C (2 mmHg); IR ν_{\max} 1740 cm⁻¹; NMR (CDCl₃) δ 7.3 (s, 5 H), 5.70 (t, CHOAc, 1 H), 2.0 (s, COCH₃, 3 H), 1.9–2.3 (m, CH, 1 H), 1.1–2.1 (m, 12 H); MS m/e 246 (M⁺), 204, 186, 149, 117, 91, 77, 43.

1-Phenyl-1,7-octadiene (7): IR ν_{\max} 3040, 1645, 910 cm⁻¹; NMR (CCl₄) δ 7.3–7.4 (m, 5 H), 4.8–6.2 (m, vinyl, 5 H), 1.8–2.4 (m, 8 H); MS m/e 186 (M⁺), 117, 104, 77, 51.

1-Phenyl-3-cyclopentylprop-1-ene (8): IR ν_{\max} 3040, 1610, 960 cm⁻¹; NMR (CCl₄) δ 7.3–7.5 (m, 5 H), 6.1–6.3 (m, vinyl, 2 H), 1.2–2.2 (m, 11 H); MS m/e 186 (M⁺), 177, 91, 77, 51.

1-Phenyl-7-octen-1-ol (9): IR ν_{\max} 3500–3400, 1645, 910 cm⁻¹; NMR (CDCl₃) δ 7.3 (s, 5 H), 5.8 (t, CHO, 1 H), 4.8–6.1 (m, vinyl, 3 H), 1.2–2.0 (m, 10 H); MS m/e 204 (M⁺), 186, 115, 105, 104, 91, 77.

1-Phenyl-3-cyclopentylpropan-1-ol (10): IR ν_{\max} 3500–3400 cm⁻¹; NMR (CDCl₃) δ 7.3 (s, 5 H), 5.9 (t, CHO, 1 H), 1.4–2.2 (m, 13 H); MS m/e 204 (M⁺), 186, 115, 104, 91.

2-Phenyl-1,8-nonadiene (13): IR ν_{\max} 3040, 1645, 1610, 980, 950 cm⁻¹; NMR (CDCl₃) δ 7.3 (s, 5 H), 4.9–6.2 (m, vinyl, 5 H), 2.1–2.3 (m, 4 H), 1.4–2.0 (m, 6 H); MS m/e 200, 172, 117, 104, 77.

2-Phenyl-4-cyclopentyl-1-butene (14): IR ν_{\max} 3040, 1610, 960 cm⁻¹; NMR (CDCl₃) δ 7.3 (s, 5 H), 5.3–5.6 (m, vinyl, 2 H), 2.2–2.0 (m, 3 H), 1.2–1.9 (m, 10 H); MS m/e 200, 199, 117, 104, 77.

Decane-1,9-dien-3-yl Acetate (15): IR ν_{\max} 1745, 1150, 910, 895 cm⁻¹; NMR (CCl₄) δ 4.9–6.0 (m, vinyl, 6 H), 4.6 (t, CH, 1 H), 2.5 (s, COCH₃, 3 H), 1.3–2.3 (m, 10 H); MS m/e 196 (M⁺), 154, 113, 99, 83, 60, 43.

5-Cyclopentyl-1-penten-3-yl Acetate (16): IR ν_{\max} 1745, 895 cm⁻¹; NMR (CCl₄) δ 5.0–6.0 (m, vinyl, 3 H), 4.7 (t, CHO, 1 H), 2.5 (m, CHC, 1 H), 1.2–2.1 (m, 12 H); MS m/e 196 (M⁺), 154, 113, 99, 83, 43.

2,9-Decadien-1-yl Acetate (17): IR ν_{\max} 1750, 1150, 910, 975 (C=C trans) cm⁻¹; NMR (CDCl₃) δ 4.9–6.2 (m, vinyl, 5 H), 3.5 (t, CHO, 2 H), 2.4 (s, COCH₃, 3 H), 2.0–2.5 (m, CH₂C=C, 4 H), 1.4–1.9 (m, 6 H); MS m/e 196, 154, 113, 60, 43.

5-Cyclopentyl-2-penten-1-yl Acetate (18): IR ν_{\max} 1745, 975 cm⁻¹; NMR (CDCl₃) δ 5.0–6.0 (m, vinyl, 2 H), 3.5 (t, CHO, 2 H), 2.4 (s, COCH₃, 3 H), 1.4–2.6 (m, 13 H); MS m/e 196 (M⁺), 154, 113, 70, 43.

4-Phenyl-2-(6-heptenyl)butanolide (25a): IR ν_{\max} 1780, 1645, 1160, 910 cm⁻¹; NMR (CDCl₃) δ 7.4 (s, 5 H), 4.9–5.1 (m, vinyl,

3 H), 5.45 (dd, CHAr, 1 H), 2.8 (dd, CHCO, 1 H), 1.9–2.2 (m, 4 H), 1.3–1.9 (m, 8 H); MS *m/e* 258 (M⁺), 240, 229, 143, 129, 117, 104, 91, 67.

4-Phenyl-2-(6-heptenyl)-2-methylbutanolide (25b): IR ν_{\max} 1785, 910 cm⁻¹; NMR (CDCl₃) δ 7.3 (s, 5 H), 4.9–5.9 (m, vinyl, 3 H), 5.2 (dd, CHO, 1 H), 2.1 (s, CH₃, 3 H), 1.1–2.4 (m, 12 H); MS *m/e* 272 (M⁺), 254, 243, 159, 117, 104, 91.

1-Phenyl-3-cyano-9-decen-1-yl Acetate (25c): IR ν_{\max} 2250, 1745, 910 cm⁻¹; NMR (CDCl₃) δ 7.3 (s, 5 H), 5.83 (t, CHAr, 1 H), 4.8–5.8 (m, vinyl, 3 H), 2.6 (quintet, CHCN, 1 H), 2.4 (td, CHC=C, 2 H), 2.5 (s, COCH₃, 3 H), 1.0–2.0 (m, 10 H); MS *m/e* 299 (M⁺, small) 257, 149, 117, 107, 104, 77, 43.

Methyl 2-(6-Heptenyl)-4-(acetoxy)-4-phenylbutanoate (25d): IR ν_{\max} 1750, 1740, 910 cm⁻¹; NMR (CDCl₃) δ 7.4 (s, 5 H), 4.9–5.9 (m, vinyl, 3 H), 4.2 (t, CHO, 1 H), 3.2 (s, OCH₃, 3 H), 2.5 (s, COCH₃, 3 H), 1.4–2.5 (m, 12 H); MS *m/e* 332, 300, 290, 149, 117, 104, 77.

1-Phenyl-3-acetyl-9-decen-1-ol (25e): IR ν_{\max} 3450, 1720 cm⁻¹; NMR (CDCl₃) δ 7.3 (s, 5 H), 4.8–6.0 (m, vinyl, 3 H), 5.4 (dd, CHAr, 1 H), 3.1 (broad, OH, 1 H), 3.0 (m, 1 H), 2.1 (s, CH₃, 3 H), 1.3–2.6 (m, 12 H); MS *m/e* 274 (M⁺, small), 213, 173, 91, 43.

4-Phenyl-2-(2-cyclopentylethyl)butanolide (26a): IR ν_{\max} 1780, 1160, 940 cm⁻¹; NMR (CDCl₃) δ 7.3 (s, 5 H), 5.54 (t, CHAr, 1 H), 2.6–2.9 (m, 2 H), 1.1–2.1 (m, 13 H); MS *m/e* 258 (M⁺), 257, 240, 162, 154, 136, 117, 104, 91, 82, 67, 59.

4-Phenyl-2-(2-cyclopentylethyl)-2-methylbutanolide (26b): IR ν_{\max} 1785 cm⁻¹; NMR (CDCl₃) δ 7.3 (s, 5 H), 5.4 (dd, CHAr, 1 H), 2.3 (dd, CHCO, 1 H), 1.1–2.2 (m, 12 H); MS *m/e* 272 (M⁺), 254, 159, 117, 77.

1-Phenyl-3-cyano-5-cyclopentylpentan-1-yl Acetate (26c): IR ν_{\max} 1785 cm⁻¹; NMR (CDCl₃) δ 7.3 (s, 5 H), 5.8 (t, CHO, 1 H), 2.6 (quintet, CHCN, 1 H), 2.4–2.6 (m, 2 H), 2.0 (s, COCH₃, 3 H), 1.0–2.0 (m, 14 H); MS *m/e* 299 (M⁺), 216, 148, 117, 107, 104, 77, 43.

Methyl 2-Cyclopentylmethyl-4-(acetyloxy)-4-phenylbutanoate (26d): IR ν_{\max} 1750, 1740 cm⁻¹; NMR (CDCl₃) δ 7.4 (s, 5 H), 5.7 (t, CHAr, 1 H), 3.3 (s, OCH₃, 3 H), 1.1–2.5 (m, 16 H); MS *m/e* 332, 300, 149, 117, 104, 77.

1-Phenyl-3-acetyl-5-cyclopentylpentan-1-ol (26e): IR ν_{\max} 3450, 1720 cm⁻¹; NMR (CDCl₃) δ 7.3 (s, 5 H), 4.9–6.0 (m, vinyl, 3 H), 5.8 (t, CHO, 1 H), 2.1 (s, 3 H), 1.1–2.4 (m, 16 H); MS *m/e* 274 (M⁺), 213, 173, 129, 91, 43.

Appendix A

Derivation of Eq 13. Application of the steady-state assumption for radical **2** according to Scheme I

$$d[2]/dt = k_6[1] - (k_9[\text{CH}=\text{CHPh}] + k_8[\text{Cu}^{2+}])[2] = 0$$

allows derivation of the ratio of radical **1** and **2** stationary concentrations:

$$[1]/[2] = k_9[\text{CH}_2=\text{CHPh}]/k_6 + k_8[\text{Cu}^{2+}]/k_6$$

Because the addition products **5** and **6** are formed respectively at the rates

$$\begin{aligned} \frac{d[5]}{dt} &= k_9[1][\text{CH}_2=\text{CHPh}] + \\ &\quad \frac{k_{10}k_9}{k_6}[2][\text{CH}_2=\text{CHPh}][\text{Cu}^{2+}] + \\ &\quad \frac{k_{10}k_9}{k_6}[\text{CH}_2=\text{CHPh}]^2[2] \\ d[6]/dt &= k_{10}[2][\text{CH}_2=\text{CHPh}] \end{aligned}$$

the ratio of the formation rates for products **5** and **6** is

$$\frac{d[5]}{d[6]} = \frac{k_9}{k_6}[\text{CH}_2=\text{CHPh}] + \frac{k_9k_8}{k_6k_{10}}[\text{Cu}^{2+}]$$

and under the hypothesis that $k_9 = k_{10}$, the relative yields

of **5** and **6** are given by eq 13 (*f* = final, *i* = initial):

$$\frac{[5]_f}{[6]_f} = k_9[\text{CH}_2=\text{CHPh}]_i/k_6 + k_8[\text{Cu}^{2+}]_i/k_6 \quad (13)$$

Appendix B

Derivation of Kinetic Eq 20–22. Application of the steady-state assumption for the radical **2** according to Schemes I and II gives rise to

$$d[2]/dt = k_6[1] - k_8[\text{Cu}^{2+}][2] - k_{10}[\text{CH}_2=\text{CHPh}][2] - k_{16}[\text{CH}_2=\text{CHX}][2] = 0$$

The addition products **25**, **26**, **5**, and **6** are formed respectively at the rates

$$\begin{aligned} \frac{d[25]}{dt} &= k_{15}[1][\text{CH}_2=\text{CHX}] = \\ &\quad \frac{k_8k_{15}}{k_6}[\text{CH}_2=\text{CHX}][\text{Cu}^{2+}][2] + \frac{k_{10}k_{15}}{k_6}[\text{CH}_2=\text{CHPh}] \times \\ &\quad [\text{CH}_2=\text{CHX}][2] + \frac{k_{15}k_{16}}{k_6}[\text{CH}_2=\text{CHX}]^2[2] \end{aligned}$$

$$\frac{d[26]}{dt} = k_{16}[\text{CH}_2=\text{CHX}][2]$$

$$\frac{d[6]}{dt} = k_{10}[\text{CH}_2=\text{CHPh}][2]$$

$$\begin{aligned} \frac{d[5]}{dt} &= k_9[\text{CH}_2=\text{CHPh}][1] = \\ &\quad \frac{k_8k_9}{k_6}[\text{CH}_2=\text{CHPh}][\text{Cu}^{2+}][2] + \\ &\quad \frac{k_9k_{10}}{k_6}[\text{CH}_2=\text{CHPh}]^2[2] + \\ &\quad \frac{k_9k_{16}}{k_6}[\text{CH}_2=\text{CHX}][\text{CH}_2=\text{CHPh}][2] \end{aligned}$$

and the relative yield of **25** and **26**, **5** and **6**, or **25** and **5** can be obtained by eq 20–22 under the hypotheses that $k_9 = k_{10}$, $k_{15} = k_{16}$, and $k_7 = k_8$

$$\frac{[25]_f}{[26]_f} = \frac{k_{15}}{k_6}[\text{CH}_2=\text{CHX}]_i + \frac{k_{10}}{k_6}[\text{CH}_2=\text{CHPh}]_i + \frac{k_8}{k_6}[\text{Cu}^{2+}]_i \quad (20)$$

$$\frac{[5]_f}{[6]_f} = \frac{k_{16}}{k_6}[\text{CH}_2=\text{CHX}]_i + \frac{k_{10}}{k_6}[\text{CH}_2=\text{CHPh}]_i + \frac{k_8}{k_6}[\text{Cu}^{2+}]_i \quad (21)$$

$$\frac{[25]_f}{[5]_f} = \frac{[26]_f}{[6]_f} = \frac{k_{16}}{k_{10}} \frac{[\text{CH}_2=\text{CHX}]_i}{[\text{CH}_2=\text{CHPh}]_i}$$

Registry No. 1, 16183-00-9; **5**, 70236-11-2; **6**, 70236-12-3; **7**, 70236-13-4; **8**, 70236-14-5; **9**, 70236-15-6; **10**, 70236-16-7; **11**, 70236-17-8; **12**, 70236-18-9; **13**, 70236-19-0; **14**, 70236-20-3; **15**, 70236-21-4; **16**, 70236-22-5; **17**, 70236-23-6; **18**, 70236-24-7; **25a**, 70236-25-8; **25b**, 70236-26-9; **25c**, 70236-27-0; **25d**, 70236-28-1; **25e**, 70236-29-2; **26a**, 70236-30-5; **26b**, 70236-31-6; **26c**, 70236-32-7; **26d**, 70236-33-8; **26e**, 70236-34-9; α -methylstyrene, 98-83-9; styrene, 100-42-5; butadiene, 106-99-0; methyl acrylate, 96-33-3; α -methacrylic acid, 79-41-4; acrylic acid, 79-10-7; methyl vinyl ketone, 78-94-4; acrylonitrile, 107-13-1; *p*-benzoquinone, 106-51-4; **2**, 23907-66-6; **20a**, 68861-90-5; **20b**, 68861-91-6; di-6-heptenyl peroxide, 26841-80-5; dicyclopentylacetyl peroxide, 26841-81-6; 2-cyclopentaneacetic acid, 1123-00-8.