Effect of Substituents on Ring Size in Radical Cyclizations. 1. Methyl vs. Phenyl[1]

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Mechanisms in cyclization of radicals (e.g., those involved in cyclopolymerization of 1,6-dienes) have been examined. The products obtained from the reactions of tributyltin hydride (Bu_3SnH) with 5,6-unsaturated hexyl radicals substituted at the 5 position were studied. The 2-allyloxyethyl radicals substituted at the 5 position were studied. The 2-allyloxyethyl radical gave 3-methyltetrahydrofuran as the only cyclic product; the 2-methallyloxyethyl radical cyclized to give up to 3% 3-methyltetrahydropyran in addition to 3,3-dimethyltetrahydrofuran and ethyl methallyl ether; 3-phenyltetrahydropyran was the predominant cyclic product from the 2-(2-phenylallyloxy)-ethyl radical. These observations support a mechanism involving classical radical cyclizations. The kinetic treatment for a reaction scheme involving competition between irreversible cyclization and abstraction of hydrogen by the initially formed radical satisfactorily fits the data. The irreversibility of the cyclization reactions was shown by generating the corresponding radical from 3-phenyl-3-bromomethyltetrahydrofuran to yield 3-phenyl-3-methyltetrahydrofuan as the only product. Thus, the kinetic treatment is also in agreement with a simple competition between irreversible cyclization reactions and abstraction of hydrogen by the acyclic radical. The rate constants and activation energies for the competing reactions were obtained from the kinetic data.

Introduction

Radical cyclizations via intramolecular attack of a radical species on an olefinic double bond have been known and studied since the initial observation was made[2] that certain 1,6-dienes polymerized via free-radical initiators to yield soluble, linear, and saturated polymers. These results could be accounted for reasonably only on the basis of an alternating intra–intermolecular chain propagation.[3] This proposal is consistent with "head to tail" enchainment in radical-initiated polymerization of vinyl monomers.[4] However, in 1961 Miyake[5] reported that the cyclic polymer obtained from poly(divinylformal) via hydrolysis contained considerable 1,2-glycol content, a structure which could reasonably arise only through five-membered rings produced via "head to head" enchainment. Subsequently, many reports of radical cyclizations which apparently proceed via the less stable radical intermediate and produce the less stable cyclic structure have appeared.[6,7]

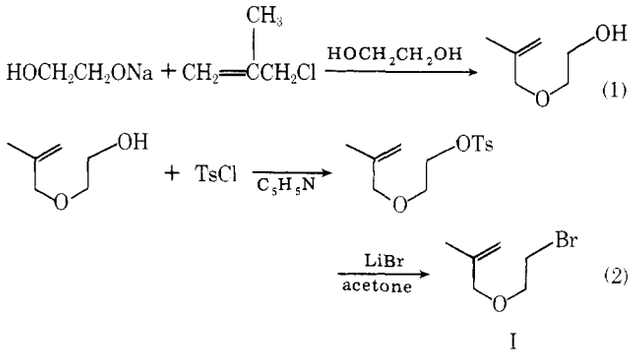
At present, no single, totally satisfactory mechanism is available which can adequately account for all of the experimental observations in these radical cyclizations.[6] Justification for apparent preference for the less-favored cyclization has been based on both electronic[8a,9] and steric[8b,10,11] factors.

Recent evidence which supports the existence of an electronic interaction in 1,5-hexadiene is based upon a photoelectron spectroscopic study[12] in which it was shown that a conformation in which the two double bonds are crossed is more stable by 2.3 kcal/mol than the open chain conformation.

Results and Discussion

It was a major purpose of this investigation to generate 5-substituted-5-hexenyl radicals in which the 5 substituent was selected from among those highly radical-stabilizing groups present in well-known vinyl monomers and to determine the ratio of five- to six-membered ring formed. Thus, 2-phenylallyl 2-bromoethyl ether, 2-methylallyl 2-bromoethyl ether, and the products which could arise from generation of the corresponding radicals in the presence of tributyltin hydride were synthesized.

Synthesis of Reactants and Predicted Products—2-Methylallyl 2-Bromoethyl Ether (I). This compound was synthesized via the reaction sequence in eq 1 and 2 utilizing well-established procedures.



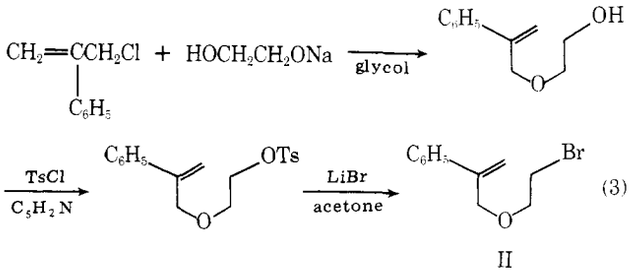
I

Ethyl methallyl ether (Ia) was prepared by treating sodium ethoxide with methallyl chloride in ethanol.

3,3-Dimethyltetrahydrofuran (Ib) was prepared from 2,2-dimethylsuccinic acid which was converted to the diethyl ester, followed by reduction of the ester to 2,2-dimethyl-1,4-butanediol with lithium aluminum hydride (LAH). The diol was converted to Ib by reaction with 60% sulfuric acid at 100 °C.

3-Methyltetrahydropyran (Ic) was prepared via a similar series of reactions beginning with 2-methylglutaric acid.

2-Phenylallyl 2-Bromoethyl Ether (II). This compound was synthesized in a manner analogous to the 2-methylallyl ether (eq 3).



II

Ethyl 2-phenylallyl ether (IIa) was prepared from the reaction of sodium ethoxide with 2-phenylallyl chloride in ethanol.

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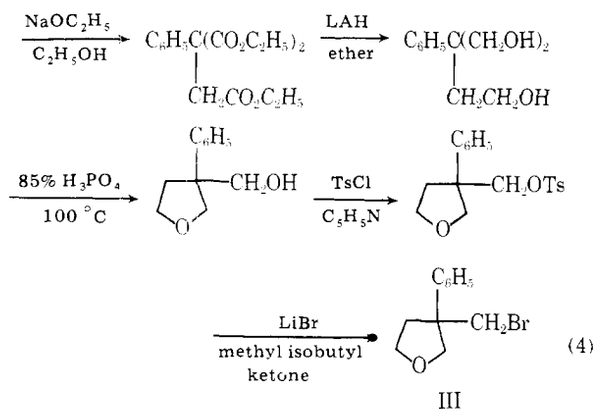
The other two expected products, 3-methyl-3-phenyltetrahydrofuran (IIb) and 3-phenyltetrahydropyran (IIc), were obtained by reacting equimolar portions of 2-bromoethyl 2-phenylallyl ether and tributyltin hydride in benzene solution in an autoclave at 130 °C. At this temperature the main products were IIb and IIc.

In order to establish the irreversibility of the reactions leading to products IIb and IIc, it was necessary to synthesize an unequivocal radical precursor to one of the radicals leading to IIb or IIc. Although cyclization of the 5-hexenyl radical had been shown to be irreversible[9,10] as well as cyclization of the 2-allyloxyethyl radical,[15] in a study of cyclization of 1-substituted 5-hexenyl radicals[7] it was shown that the cyclization reactions were reversible when C-1 was disubstituted (two -CN or $-COOC_2H_5$ groups). It was also shown[7] that as substitutions on C-1 by radical stabilizing groups (one or two -CN or $-COOC_2H_5$ groups) gradually increased, the mixture of products changed from nearly pure cyclopentane to nearly pure cyclohexane derivatives. The reaction sequence[13] in eq 4 was employed for the synthesis of 3-phenyl-3-(bromomethyl)tetrahydrofuran (III).



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Tributyltin hydride (Bu_3SnH) was prepared according to the procedure of Kuivila and Buenel[14] by reaction of tributyltin chloride with LAH.

Generation and Reactions of Radicals. The 2-Methylallyloxyethyl Radical. The techniques involved in generating the radicals and analyzing the resulting products were modeled after previously published procedures.[15,16] In all cases the molar ratio of the bromide to Bu_3SnH in the reaction mixtures was about 3:1. The amount of AIBN was 1.5 mol % based on Bu_3SnH concentration. The solutions prepared are described in Table IV. Quantitative determinations of the concentration of products resulting from the reactions of the radicals with Bu_3SnH were made by GC. The product concentrations resulting from these reaction solutions are given in Table IX. The yield percentages of the products based on the initial concentrations of the Bu_3SnH are listed in Table X. The ratio of 3,3-dimethyltetrahydrofuran to 3-methyltetrahydropyran formed at each temperature was approximately the same for all three concentrations of reactants. The ratios observed at the three reaction temperatures are listed in Table I. The results obtained with this ether are consistent with those subsequently obtained from 2-methyl-6-bromo-1-hexene.[17]

The 2-(2-Phenylallyloxy)ethyl Radical. The procedure, molar ratios of reactants, and methods of analysis were analogous to those used for the previous system.

Table XI shows the compositions of the solutions prepared to study the reactions of the 2-(2-phenylallyloxy)ethyl radical with Bu_3SnH. The product concentrations resulting from these reaction mixtures are listed in Table XII. The yield percentages of the products based on the initial concentrations of the tributyltin hydride are listed in Table XIII.

Table I. Ratios of 3,3-Dimethyltetrahydrofuran to 3-Methyltetrahydropyran Produced

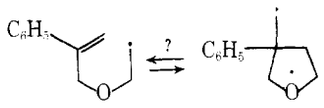
Temp, °C	[Ib]:[Ic]
40	43 ± 1.5
90	30 ± 1.0
125	24 ± 1.0

Table II. Ratios of 3-Phenyltetrahydropyran to 3-Phenyl-3-methyltetrahydrofuran Produced

Temp, °C	[IIc]:[IIb]
40	1.82 ± 0.04
90	1.92 ± 0.04
130	2.00 ± 0.05

The ratio of 3-phenyltetrahydropyran to 3-phenyl-3-methyltetrahydrofuran formed at each temperature was approximately the same for all three concentrations of reactants. The ratios observed at the different reaction temperatures are listed in Table II.

The (3-Phenyl-3-tetrahydrofuranyl)methyl Radical. The (3-phenyl-3-tetrahydrofuranyl)methyl radical was generated from 3-phenyl-3-bromomethyltetrahydrofuran under the usual reaction conditions at 90 °C to check the reversibility of its formation from the 2-(2-phenylallyloxy)ethyl radical. It was reasoned that if either of the cyclization reactions of the 2-(2-phenylallyloxy)ethyl radical was reversible, the one



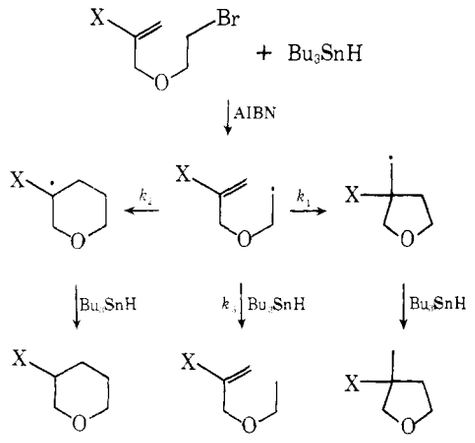
shown should be since the other radical leading to 3-phenyltetrahydropyran should be a more stable benzylic radical. The only product obtained when this bromide was treated with Bu_3SnH under the usual conditions at 90 °C was 3-phenyl-3-methyltetrahydrofuran, which proves the stability of the (2-phenyl-3-tetrahydrofuranyl)methyl radical under these conditions. Thus it appears the radical cyclization reactions of the 2-(2-phenylalloxy)ethyl radical are irreversible processes, just as they were shown to be for the cyclization reactions of the 5-hexenyl radical[9] and subsequently for the 5-methyl-5-hexenyl radical.[17]

Kinetics of the Radical Reactions. The groundwork for studying the kinetics of the reactions of radical systems of the type studied in this work was established by Walling et al.[15] and by Carlsson and Ingold.[18] The first group[15] reported a kinetic treatment for the competing reactions of the 5-hexenyl radical in the presence of Bu_3SnH. The second group[18] established the fact that for the reaction of an alkyl bromide with tributyltin hydride in the presence of a radical initiator, the rate-controlling step is abstraction of hydrogen from the tributyltin hydride by the alkyl radical. Thus, the competing reactions of the alkyl radical can be studied kinetically by this method.

Equation 5 quite satisfactorily fit the data obtained for the reaction products obtained from the 2-methyllyloxyethyl radical and the 2-(2-phenylalloxy)ethyl radical. The equation

$$-\frac{d[Bu_3SnH]}{d\left[\text{X-C(=CH}_2\text{)-CH}_2\text{-CH}_2\text{-O-C}_6\text{H}_5\right]} = \frac{k_1 + k_2 + k_3[Bu_3SnH]}{k_3[Bu_3SnH]} \quad (5)$$

Scheme I

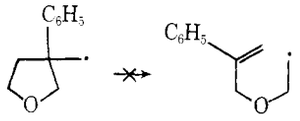


was integrated between the initial and final reaction conditions to yield eq 6.

$$\left[\text{X}\right]\text{F} = [\text{Bu}_3\text{SnH}]_\text{I}\,\frac{k_1 + k_2}{k_3}\ln\frac{k_1 + k_2 + k_3[\text{Bu}_3\text{SnH}]_\text{I}}{k_1 + k_2} \tag{6}$$

Scheme I shows the reactions of the two radical systems studied. It is analogous to the reaction scheme described for the reactions of the 4-(1-cyclohexenyl)butyl radical by Strubble, Beckwith, and Gream.[19a] As they observed a constant ratio of the spiro compound to the decalin formed over a sevenfold change in tributyltin hydride concentration, we observed a constant ratio of tetrahydrofuran derivatives to tetrahydropyran derivative over a fourfold change in tributyltin hydride concentration at each temperature for both of the radical systems studied.

Since the cyclization of the 2-(2-phenylallyloxy)ethyl radical to the 3-(2-phenyltetrahydrofuranyl)methyl radical was shown to be an irreversible process (eq 7), it would seem reasonable to assume that all four cyclic radicals formed in the two radical systems studies were formed irreversibly. The methyl analog of the five-membered cyclic radical should be no more likely to undergo the reverse reaction than the phenyl system, while the two six-membered cyclic radicals, one being tertiary and the other benzylic, should be less likely to undergo the reverse reaction.



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The lack of reversibility of the radical cyclizations coupled with the constant ratios of cyclic products at each temperature supports the proposed reaction scheme, whereby the cyclic products arise from irreversible radical cyclizations whose rates are independent of the tributyltin hydride concentration. Thus the ratio of k_1 to k_2 is just the constant ratio of tetrahydrofuran derivative to tetrahydropyran derivative formed at that temperature as shown in eq 8.

$$\frac{k_1}{k_2} = \frac{\left[\text{X}\right]}{\left[\text{X}\right]} \tag{8}$$

Using this relationship between k_1 and k_2 it was possible to solve eq 6 by trial and error for a value of k_3/k_1 or k_3/k_2 which would fit each set of data. The values of k_3/k_1 or k_3/k_2 which gave the best fit for the products obtained from the 2-methyllyloxyethyl radical and the 2-(2-phenylallyloxy)ethyl radical, respectively, are listed in Table III. Also listed in Table III are the values of $[\text{Ia}]_\text{calcd}$ and $[\text{IIa}]_\text{calcd}$, the calculated values of the concentration of uncyclized product, which are obtained when the k_3/k_1 or k_3/k_2 which best fits the data is plugged into eq 3.

Table III. Values of k_3/k_1 or k_3/k_2 Which Best Fit the Data According to Eq 6

2-Methallyloxyethyl Radical System

Solution	Temp, °C	$[\text{Ia}]_\text{obsd}$	k_3/k_1	$[\text{Ia}]_\text{calcd}$
41	40	0.0042	16.4	0.0043
42	40	0.0134	16.4	0.0132
43	40	0.0400	16.4	0.0402
91	90	0.0028	9.9	0.0027
92	90	0.0088	9.9	0.0090
93	90	0.0300	9.9	0.0298
121	125	0.0020	7.6	0.0020
122	125	0.0077	7.6	0.0074
123	125	0.0250	7.6	0.0252

2-(2-Phenylallyloxy)ethyl Radical System

Solution	Temp, °C	$[\text{IIa}]_\text{obsd}$	k_3/k_2	$[\text{IIa}]_\text{calcd}$
401	40	0.0021	10.4	0.0021
402	40	0.0070	10.4	0.0069
403	40	0.0242	10.4	0.0244
901	90	0.0016	7.6	0.0016
902	90	0.0055	7.6	0.0054
903	90	0.0195	7.6	0.0197
131	130	0.0012	5.9	0.0012
132	130	0.0050	5.9	0.0050
133	130	0.0155	5.9	0.0157

Table IV. Composite of Rate Constant Ratios

Radical	Temp, °C	k_1/k_2	k_3/k_1	k_3/k_2
2-Methallyloxyethyl	40	43	16.5	710
	90	30	9.9	297
	125	24	7.6	182
2-(2-Phenylallyloxy)ethyl	40	0.55	18.9	10.4
	90	0.52	14.6	7.6
	130	0.50	11.8	5.9

From Table III it can be seen that a single value of k_3/k_1 or k_3/k_2 gives a good fit of the data to eq 3 at each temperature. The particular value of k_3/k_1 or k_3/k_2 which best fits the results from a single reaction solution to eq 3 is no more than 3% away from the value which gives the best overall fit for the data at that temperature.

The values of k_1/k_2, k_3/k_1, and k_3/k_2 which were obtained for the two radical systems at each of the three reaction temperatures are collected in Table IV.

Applying the Arrhenius equation to these ratios of rate constants gives eq 9 and 10.

$$k_1/k_2 = (A_1/A_2)\quad \exp\left(\frac{E_{A_2} - E_{A_1}}{RT}\right) \tag{9}$$

$$\ln(k_1/k_2) = \ln(A_1/A_2) + \frac{E_{A_2} - E_{A_1}}{RT} \tag{10}$$

Plots of $\ln(k_1/k_2)$ vs. $1/T$ gave straight lines with slopes of $(E_{A_2} - E_{A_1})/R$ and intercepts of $\ln(A_1/A_2)$. The values of the various activation energy differences and frequency factor ratios obtained from the slopes and intercepts are listed in Table V. The margins of error listed in the table were obtained

Table V. Activation Energy Differences and Frequency Factor Ratios

Property	2-Methallyloxyethyl radical	2-(2-Phenylallyloxy)ethyl radical
$E_{A_2} - E_{A_1}$ (kcal/mol)	1.7 ± 0.15	0.26 ± 0.05
$E_{A_1} - E_{A_3}$ (kcal/mol)	2.2 ± 0.15	1.3 ± 0.25
$E_{A_2} - E_{A_3}$ (kcal/mol)	3.9 ± 0.3	1.6 ± 0.25
A_2/A_1	0.35 ± 0.08	2.8 ± 0.2
A_3/A_1 (L/mol)	0.44 ± 0.07	2.3 ± 0.8
A_3/A_1 (L/mol)	1.3 ± 0.55	0.85 ± 0.25

graphically from the two most extreme lines which could be drawn through the limits of the three points. The ranges of the points were determined from the ranges of the rate constant ratios which gave the best fit of the data to eq 6, considering the product concentrations in the reaction mixtures were within about 2% of the measured values.

The product distributions from the 2-methallyloxyethyl radical (Table X) show that up to 3% of 3-methyltetrahydropyran (Ic) was formed in addition to the two major products. In the case of the 2-(2-phenylallyloxy)ethyl radical, 3-phenyltetrahydropyran (IIc) was the predominant cyclic product, indicating that the increased stability of the benzylic radical intermediate is the major controlling factor in the product distribution.

The kinetic results show that Scheme I quite adequately describes the reactions of the two radicals studied in this research. Equation 6, which was derived from this scheme, gave a good fit to the data for both radical systems at all three temperatures. The formation of the cyclic products can be accounted for by irreversible cyclizations of the initially formed radicals—processes whose rates are independent of the Bu_3SnH concentrations. The irreversibility of the cyclizations was checked by generating the (3-phenyl-3-tetrahydrofuranyl)methyl radical from the corresponding bromide. 3-Phenyl-3-methyltetrahydrofuran was the only product formed.

From the kinetic results it was possible to get an estimate of the activation energies for the cyclization reactions relative to the activation energy for the abstraction of hydrogen from Bu_3SnH by a primary alkyl radical. Wilt, Massie, and Dabek[16] have calculated the activation energy for this hydrogen abstraction process to be between 6.8 and 8.2 kcal/mol using rate constants reported by Carlsson and Ingold.[18] The comparisons of the rate constants for the cyclization reactions to that for the hydrogen abstraction from Bu_3SnH by the initially formed primary alkyl radicals were presented in Table V. The rate constants for hydrogen abstraction by the 2-methyloxyethyl and the 2-(2-phenylallyloxy)ethyl radical should be very nearly the same. Thus it is possible to compare the activation energies for the cyclization reactions leading to the four cyclic products in the two radical systems. The order of activation energies for the four cyclizations is presented in Table VI in relation to E_4(H), the activation energy for the hydrogen abstraction by the initially formed primary radicals.

These values show that the activation energy for the cyclization of the 2-(2-phenylallyloxy)ethyl radical to form 3-phenyltetrahydropyran is about 2.3 kcal/mol less than the activation energy for the cyclization of the 2-methyllyloxyethyl radical to form 3-methyltetrahydropyran. This helps to explain why formation of the six-membered cyclic product competes so much more favorably in the phenyl system than in the methyl system.

The relationships between the three rate constants in both of the radical systems were established. Approximate values of the rate constants for the cyclization reactions of the two radicals were obtained from the rate constant relationships and the reported value[18] of the rate constant for abstraction

Table VI

Product	$E_A - E_A$ (H), (kcal/mol)
3-phenyl-3-methyltetrahydrofuran	1.3 ± 0.25
3-Phenyltetrahydropyran	1.6 ± 0.25
3,3-Dimethyltetrahydrofuran	2.2 ± 0.15
3-Methyltetrahydropyran	3.9 ± 0.3

Table VII

Product	k_c, s^{-1} at 40 °C
3-Phenyltetrahydropyran	9.6×10^4
3,3-Dimethyltetrahydrofuran	6.1×10^4
3-Phenyl-3-methyltetrahydrofuran	5.3×10^4
3-Methyltetrahydropyran	1.4×10^3

of hydrogen from tributyltin hydride by the 1-hexyl radical ($k = 1.0 \times 10^6$ M^{-1} s^{-1} at 25 °C). Comparing this value to the ratios reported in Table IV gives the values listed in Table VII for the rate constants of the four cyclization reactions at 40 °C.

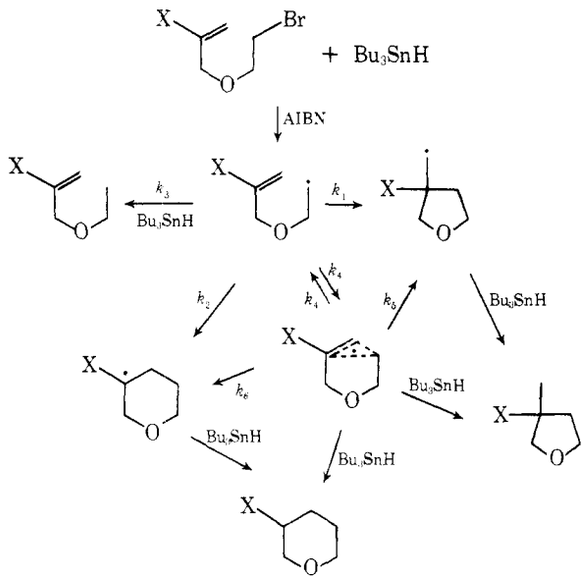
The total rate constant for cyclization in either of the two radical systems would be simply $k_1 + k_2$, the sum of the two rate constants for the cyclization reactions. The approximate values for the methyl and phenyl systems studied in this work are 6.2×10^4 and 1.5×10^5 s^{-1}, respectively. The fact that this total rate constant for cyclization is more than twice as great for the phenyl system as for the methyl system appears to arise from the differences in rate constants for cyclization to the tetrahydropyran derivatives. The rate constants for formation of the tetrahydrofuran derivatives are nearly the same. This big difference is likely due to the greater stability of the benzylic radical leading to 3-phenyltetrahydropyran compared to the tertiary radical leading to 3-methyltetrahydropyran

Carlsson and Ingold[18] determined the rate constants for cyclization at 40 °C for the 1-hexenyl radical studied by Walling et al.[15] and for the 4-(1-cyclohexenyl)butyl radical reported by Strubble, Beckwith, and Gream[19a] by comparing the reported rate constant ratios with the rate constant for hydrogen abstraction from Bu_3SnH by the 1-hexyl radical at 25 °C. The values of k_c obtained were 1×10^5 s^{-1} for the 5-hexenyl radical and 4×10^4 s^{-1} for the 4-(1-cyclohexenyl)butyl radical. In a recent elegant paper by Lal et al.,[20] the rate constant k_c for the 1-hexenyl radical was confirmed by an EPR spectroscopic technique. They compared these constants with the rate constant for addition of an ethyl radical to 1-heptene at 40 °C, 1×10^3 M^{-1}, and stated that the "effective double bond concentration" for the intramolecular cyclization of such radicals is about 40 to 100 M. Such a comparison with the cyclization rate constant for the 2-methyllyloxyethyl radical yields a value of 62 M. For the 2-(2-phenylallyloxy)-ethyl radical the value would be 150 M, but a more accurate basis for comparison would be with the rate constant for addition of a primary radical to an α-alkyl styrene, which should have a value greater than 1×10^3 M^{-1} s^{-1} at 40 °C.

This enhanced "effective double bond concentration" for reaction of the initial radical with the double bond to give a cyclic radical, coupled with the increased steric hindrance to approach of another monomer molecule when the initial radical is part of a growing polymer chain, should be sufficient to explain why so many 1,6-dienes undergo free-radical polymerization to yield polymers composed entirely of cyclic repeating units. Propagation by reaction of the initial radical with another molecule of monomer simply cannot compete with the cyclization processes in most cases.

The products obtained from the reactions of the two radi-

Scheme II



cals studied in this work were consistent with a reaction scheme whereby the cyclic products arise from irreversible radical cyclizations. The kinetic treatment further supports this explanation. Equation 6, when applied to the data of Strubble, Beckwith, and Gream[19a] for the products from reactions of the 4-(1-cyclohexenyl)butyl radical with tributyltin hydride at 40 °C, gave a good fit for $k_3/(k_1 + k_2) = 40$. Equation 6 also gave a good fit to the data reported by Beckwith and Gara[19b] for the reactions of the 2-(3-butenyl)phenyl radical with Bu_3SnH with $k_3/k_c = 2.0$. The data of Walling et al.[15] for the reactions of the 5-hexenyl radical with Bu_3SnH at 40 °C were satisfied by eq 6 with $k_3/k_c = 10$. Only Walling's data at 130 °C, which showed no distinct trend in product distribution, failed to satisfactorily fit eq 6.

From our results and the results of other studies on similar radical systems, it would appear that a reaction path involving a complex between the radical and the double bond is not necessary to explain the formation of the cyclic products. Scheme I involving a competition between the simple irreversible radical reactions leading to the cyclic and noncyclic products satisfactorily explains the observed product distributions. However, the possibility of the presence of a radical-π complex at some point in the reaction cannot be ruled out. Participation of such a complex is considered in Scheme II. It is possible that a complex is formed reversibly from the uncyclized radical and then collapses irreversibly to the cyclic radicals. The fact that 3-phenyl-3-methyltetrahydropyran was the only product obtained from the (3-phenyl-3-tetrahydrofuranyl)methyl radical shows that such a transformation from a complex to the cyclic radical, if it is involved, is irreversible. A direct route from complex to cyclic products is possible if the rate-determining step is formation of the complex rather than attack of the complex by the tributyltin hydride. The steric factors, if important enough in view of the electronic factors involved, would discount the last possibility since the products obtained were not those expected from attack on a complex by the hydride at the more accessible position. Beckwith et al.[21] have recently studied the effects of substituents at C-6 on the rate of 1,6-cyclization of radicals. However, these authors point out that their data do not permit the effects to be accurately assessed, but they do state that "it appears that steric factors are much more important than electronic factors in influencing the rate of intramolecular addition." Some of these problems might be answered by a study of a similar system with a bulky alkyl group on the double bond.

The fact that the cyclic radicals were found to form irreversibly discounts the possibility of the cyclized radicals being in equilibrium with a complex. If such a complex were low in energy relative to the cyclic radicals, one might expect the cyclic radicals to revert to the complex form and partition themselves between the two cyclic products and perhaps also the uncyclized product. The results of Kochi and Krusic[22] also cast some doubt as to the formation of a nonclassical radical species in radical cyclizations of this type. By ESR studies they were able to see the 5-hexenyl radical and the cyclopentylmethyl radical but no other in between. However, more recent ESR results on this radical by Edge and Kochi[23] have led to the postulate that the drastic line broadening due to the β-proton triplets may be associated with a coiled conformation in which the terminal unsaturated system lies over the radical center, thus supporting the nonclassical radical species or the complex.

The proportions of five-membered and six-membered cyclic products in the two radical systems studied appeared to be dependent upon the activation energies for the competing cyclization reactions and also upon steric factors concerning the ease of approach of the radical to the two ends of the double bond. These effects would also be important in determining the ring size of the repeating units of cyclopolymers. When the initial radicals are stable enough that the radical cyclization reactions are partially or totally reversible, as in the case of some of the radical systems studied by Julia,[7] the stabilities of the cyclized radicals become an additional factor in determining the proportions of five-membered and six-membered cyclic repeating units in cyclopolymers.

Experimental Section

Equipment and Data. All temperatures are reported uncorrected in °C. Nuclear magnetic resonance (NMR) spectra were obtained on a Varian A-60A Analytical NMR spectrometer. Infrared (IR) spectra were obtained with a Beckman IR-8 infrared spectrophotometer. Refractive indices were obtained with a Bausch and Lomb Abbé 34 refractometer equipped with an anchromatic compensating prism. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Ga., and by PCR, Inc., Gainesville, Fla. Gas chromatographic (GC) analyses were done on a Hy-Fi Aerograph Model 600-D gas chromatograph. Preparative scale GC was done on an F & M Model 775 Prepmaster gas chromatograph. The reactions were run in sealed, degassed tubes in a constant-temperature bath controlled by a Sargent Thermonitor to within ±0.01 °C. Bu_3SnH was prepared according to the procedure of Kuivila and Buemel.[14]

Preparation of 2-Methylallyloxyethanol. The procedure of Hurd and Pollack[24] was followed and the reaction was carried out on a 0.5 mol scale: yields, 45.5 g (82%) of 2-methallyloxyethanol; bp 163 °C (760 mm) (lit.[25] bp 172 °C (760 mm)); n^{24}D 1.4386 (lit.[25] n^{25}D 1.4372). NMR and IR spectra confirmed the proposed structure.

Preparation of I. The above procedure[24] was followed and the reaction was carried out on a 0.25 mol scale: yield, 4.8 g (11%); bp 75–76 °C (25 mm); n^{25}D 1.4655. NMR and IR spectra confirmed the proposed structure.

Anal. Calcd for $C_6H_{11}BrO$: C, 40.24; H, 6.19; Br, 44.63. Found: C, 40.36; H, 6.08; Br, 44.99.

Preparation of 2-Methyllyloxyethyl *p*-Toluenesulfonate. The procedure of Ansell[26] was used: yield, 39.0 g (74%). This previously unreported compound was identified by its IR and NMR spectra.

Preparation of I from 2-Methyllyloxyethyl *p*-Toluenesulfonate. The procedure reported by Wilt, Massie, and Dabek[16] was employed on a 0.14 mol scale: yield, 17.1 g (68%); bp 70–71 °C (20 mm); n^{26}D 1.4651. The product was shown to be pure by GC. The structure was confirmed by refractive index, IR, and NMR.

Preparation of Ia via the Williamson Synthesis. Ia was prepared according to a literature procedure[27] on a 1.0 mol scale: yield, 55.0 g (55%); bp 86.5 °C (760 mm) (lit.[27] bp 84.8–86.8 °C (760 mm)); n^{25}D 1.3970 (lit.[27] n^{20}D 1.4067). GC, NMR, and IR confirmed purity and structure.

Preparation of Diethyl 2-Methylglutarate. A procedure in "Organic Syntheses" [28] for the esterification of dicarboxylic acids was used on a 0.33 mol scale: yield, 64.1 g (96%); bp 128 °C (20 mm) (lit.[29] bp 125 °C (20 mm)); n^{26}D 1.4230 (lit.[29] n^{20}D 1.4265). NMR and IR confirmed the structure.

Preparation of Diethyl 2,2-Dimethylsuccinate. The procedure in ref 28 was used on a 1.0 mol scale: yield, 54.0 g (81%); bp 107 °C (15 mm) (lit.[30] bp 102 °C (15 mm)); n^{25}D 1.4201 (lit.[30] n^{20}D 1.4233). NMR and IR confirmed the structure.

Preparation of 2-Methyl-1,5-pentanediol. A procedure in Vogel's "Textbook of Practical Organic Chemistry" [31] for reducing esters to alcohols was followed on a 0.25 mol scale: yield, 19.9 g (68%); bp 135–136 °C (6 mm) (lit.[29] bp 140 °C (20 mm)); n^{25}D 1.4524 (lit.[29] n^{20}D 1.4545). NMR (D_2O) and IR confirmed the structure.

Preparation of 2,2-Dimethyl-1,4-butanediol. The procedure for preparing 2-methyl-1,5-pentanediol[31] was used on a 0.25 mol scale by reduction of diethyl 2,2-dimethylsuccinate: yield, 12.3 g (42%); bp 163 °C (15 mm) (lit.[30] bp 117 °C (8 mm)); n^{25}D 1.4436 (lit.[30] n^{20}D 1.4513). NMR (D_2O) and IR confirmed the structure.

Preparation of Ic. Into a pressure bottle were charged 30 g of 60% sulfuric acid and 10.0 g (0.085 mol) of 2-methyl-1,5-pentanediol. The liquids were heated to 100 °C for 1 h, then cooled overnight. The bottle was opened and the contents were diluted with 30 mL of water and distilled. The product and water distilled as an azeotrope, and 7.5 g of crude product was obtained which was dried over 3A molecular sieves. After two distillations through a 60-cm spinning-band column with Teflon band the yield was 3.8 g (45%) of a clear, colorless, volatile liquid: bp 108 °C (760 mm) (lit.[29] bp 109 °C (733 mm)); n^{25}D 1.4194 (lit.[29] n^{20}D 1.4210). NMR, IR, and GC confirmed the identity and purity. An impurity present in the original mixture was identified by NMR to be 2,2-dimethyltetrahydrofuran, which could have resulted from a 1,2-hydride shift to form a tertiary carbonium ion prior to cyclization.

Preparation of Ib. The same general technique as for the synthesis of 3-methyltetrahydropyran was used. From 6.0 g (0.051 mol) of 2,2-dimethyl-1,4-butanediol was obtained 4.8 g (94%) of product: bp 99 °C (760 mm) (lit.[30] bp 98–99 °C (750 mm)); n^{25}D 1.4102 (lit.[30] n^{20}D 1.4121). GC, NMR, and IR confirmed the purity and identity of the structure.

Preparation of 2-(2-Phenylallyloxy)ethanol. The procedure of Hurd and Pollack[24] was employed on a 0.5 mol scale: yield, 59.3 g (67%); bp 109–111 °C (0.5 mm); n^{27}D 1.5456. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.96; H, 8.12. NMR and IR confirmed the identity of the structure.

Preparation of 2-(2-Phenylallyloxy)ethyl *p*-Toluenesulfonate. The procedure of Ansell[26] was used on a 0.1 mol scale with slight modifications. The reaction mixture was left at room temperature overnight before being worked up. The product was shown by thin-layer chromatography to consist of two major components. They were separated by column chromatography using silica gel and a solvent system of 85% petroleum ether (65–110 °C) and 15% ethyl ether. The two separated components were identified as the expected *p*-toluenesulfonate and 2-phenylallyl 2-chloroethyl ether. Formation of the chloride is not surprising. It has been stated by Fieser and Fieser[32] that in the presence of pyridinium chloride at room temperature primary tosylates are converted to chlorides. Thus the reaction mixture should not be allowed to exceed 20 °C. The chloride was distilled through a 16-cm Vigreux column: yield, 5.2 g (26.5%); bp 88 °C (0.25 mm); n^{25}D 1.5428. NMR and IR confirmed the identity of the structure. Anal. Calcd for $C_{11}H_{13}ClO$: C, 67.17; H, 6.66; Cl, 18.03. Found: C, 67.23; H, 6.69; Cl, 17.86.

The *p*-toluenesulfonate was obtained in a yield of 6.3 g (19%).

Another procedure[33] provided a good yield of the desired 2-(2-phenylallyloxy)ethyl *p*-toluenesulfonate from the alcohol. The reaction was carried out on a 0.10 mol scale: yield, 29.7 g (89%). NMR and IR confirmed the structure.

Preparation of II via 2-(2-Phenylallyloxy)ethyl *p*-Toluenesulfonate. The procedure of Wilt, Massie, and Dabek[16] was employed on a 0.09 mol scale: yield, 18.9 g (88%); bp 98 °C (0.2 mm); n^{25}D 1.5593. NMR and IR confirmed the assigned structure. Anal. Calcd for $C_{11}H_{13}BrO$: C, 54.79; H, 5.43; Br, 33.14. Found: C, 54.85; H, 5.51; Br, 32.97.

Preparation of IIa via the Williamson Synthesis. The procedure by Baucom[34] was used. The reaction was carried out on a 0.20 mol scale: yield, 14.7 g (45%); bp 99.5 °C (10 mm) (lit.[35] bp 96 °C (10 mm)); n^{25}D 1.5215 (lit.[35] n^{25}D 1.5202). GC, NMR, and IR confirmed the identity and purity of the product.

Preparation of IIb and IIc via Cyclization of II. A solution of 6.03 g (0.025 mol) of 2-bromoethyl 2-phenylallyl ether, 7.55 g (0.026 mol) of Bu_3SnH, and 0.062 g (0.0004 mol) of AIBN in 500 mL of spectrograde benzene was sealed in an autoclave (1-L capacity). The contents were run through three freeze–thaw cycles using a vacuum system (0.02 mm) and a dry ice–isopropyl alcohol bath. Then they were placed in a preheated cavity and heated at 130 °C for 3 h. The contents were allowed to cool and most of the benzene was removed on a rotary evaporator. The remaining benzene was removed by distillation at atmosphereic pressure. The residue was distilled at a pressure of 7.5 mm to separate the more volatile products from the tributyltin bromide. The two major products, 3-phenyltetrahydropyran and 3-methyl-3-phenyltetrahydrofuran, were isolated by means of preparative GC using an F & M Model 775 Prepmaster GC with an 8 ft × ¾ in. column of 20% SE-30.

Pure IIb was isolated in 17.5% yield (0.7 g): bp 101 °C (4 mm); n^{25}D 1.5271. NMR and IR confirmed its identity. Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.57; H, 8.70.

Pure IIc was isolated in 35% yield (1.4 g): bp 104 °C (4 mm); n^{25}D 1.5295 (lit.[36] n^{25}D 1.5267). NMR and IR confirmed the identity of this structure.

Preparation of Triethyl 2-Phenyl-2-carboxysuccinate. The standard procedure for malonic ester syntheses was used on a 0.61 mol scale: yield, 116.5 g (59%); bp 164–165 °C (1.2 mm); n^{26}D 1.4904. NMR and IR confirmed the identity of this compound. Anal. Calcd for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88. Found: C, 63.45; H, 6.96.

The by-product, ethyl ethoxyacetate, was obtained as a clear, colorless liquid: bp 34 °C (2.2 mm) (lit.[37] bp 55 °C (11 mm)); n^{25}D 1.4031 (lit.[37] n^{25}D 1.4019); yield, 27 g (33.5%). NMR and IR confirmed the identity of this by-product.

Preparation of 2-Phenyl-2-hydroxymethyl-1,4-butanediol. The procedure described[13] for LAH reductions of esters was employed using 0.276 mol of triethyl 2-phenyl-2-carboxysuccinate: yield, 47.1 g (88%). Distillation was not attempted since it is stated that the triol is not stable to distillation.[13] NMR and IR confirmed the identity of the triol.

Preparation of 3-Phenyl-3-hydroxymethyltetrahydrofuran. The procedure described[13] for the cyclization was used on 26.0 g (0.13 mol) of 2-phenyl-2-hydroxymethyl-1,4-butanediol and 67 g (0.58 mol) of 85% phosphoric acid. Distillation of the crude liquid yielded 12.1 g of a viscous liquid which was shown by IR, NMR, and GC to be a mixture containing about 75% of the desired product. The product was redistilled through a 40-cm heated column packed with saddles, yielding three fractions containing about 80%, 88%, and 92% product according to the gas chromatographs. The yields of these three fractions were 6.0, 3.5, and 0.6 g, respectively (37%). Further purification was not attempted since it was planned to make the tosylate, which could be purified and identified: bp 93–94 °C (0.05 mm) (lit.[13] bp 119–120 °C (0.6 mm)); n^{25}D 1.5496 (lit.[13] n^{25}D 1.5471).

Preparation of 3-(3-Phenyltetrahydrofuranyl)methyl *p*-Toluenesulfonate. The procedure for the preparation of 2-(2-phenylallyloxy)ethyl *p*-toluenesulfonate was followed,[33] using 6.65 g (0.033 mol) of 88% 3-phenyl-3-hydroxymethyltetrahydrofuran, 10.5 g (0.13 mol) of pyridine, and 8.4 g (0.044 mol) of *p*-toluenesulfonyl chloride: yield, 8.5 g (77%); mp 115 °C (lit.[13] mp 104 °C). NMR and IR confirmed the identity of the product. Anal. Calcd for $C_{18}H_{20}SO_4$: C, 65.04; H, 6.06; S, 9.65. Found: C, 64.88; H, 6.19; S, 9.50.

Preparation of 3-Phenyl-3-bromomethyltetrahydrofuran. The procedure[16] described earlier was employed, using 8.3 g (0.025 mol) of 3-(3-phenyltetrahydrofuranyl)methyl *p*-toluenesulfonate and 7.0 g (0.080 mol) of anhydrous lithium bromide in 150 mL of methyl isobutyl ketone: yield, 5.2 g (87%); bp 92–93 °C (0.07 mm); n^{25}D 1.5676. NMR and IR confirmed the identity of the product. Anal. Calcd for $C_{11}H_{13}BrO$: C, 54.79; H, 5.43; Br, 33.14. Found: C, 54.85; H, 5.43; Br, 33.24.

Preparation and Analysis of Reaction Solutions. Reactions of I and Bu_3SnH. The solutions for study of the reactions of 2-bromoethyl methallyl ether with Bu_3SnH were prepared in the following manner: AIBN, which had been recrystallized from methanol, was weighed out first and set aside. Bu_3SnH, freshly prepared and stored in an airtight container under N_2, was weighed in a volumetric flask and diluted with spectrograde benzene. Then the 2-bromomethyl methallyl ether, which was free of impurities according to GC, was weighed in the volumetric flask and the flask was filled to the mark with spectrograde benzene. The AIBN was added and the solution was shaken and transferred to reaction tubes. The tubes were degassed by three freeze–thaw cycles, sealed, and heated at the desired reaction temperature until the reactions had reached completion.

The product distributions resulting from the various reactions were analyzed by GC on a Hy-Fi Aerograph, using a 9-ft β,β′-oxydipropionitrile column at 50–55 °C with the injection temperature at 185 °C. Calibration curves for concentration vs. peak area were prepared for the reaction products using standard solutions of mixtures of the authentic products in benzene. The accuracy of these determinations was checked often by preparing solutions containing the concentrations of the three products in the reaction mixture according to the calibration curve. In this manner slight errors could be corrected and the calibration could be checked often.

Table VIII. Reaction Solutions for Generation and Reactions of 2-Methallyloxyethyl Radical

Solution	Temp, °C	[Bu_3SnH]	[I]	[AIBN]
41	40	0.0262	0.0764	0.0004
42	40	0.0497	0.1495	0.0008
43	40	0.0998	0.3014	0.0015
91	90	0.0262	0.0764	0.0004
92	90	0.0497	0.1495	0.0008
93	90	0.0998	0.3014	0.0015
121	125	0.0248	0.0743	0.0004
122	125	0.0502	0.1484	0.0008
123	125	0.1007	0.3046	0.0017

Table IX. Product Concentrations from Reactions of the 2-Methallyloxyethyl Radical[a]

Solution	Temp, °C	[Ia]	[Ib]	[Ic]
41	40	0.0042	0.0197	0.00045
42	40	0.0134	0.0320	0.00075
43	40	0.0400	0.0470	0.0011
91	90	0.0028	0.0210	0.00070
92	90	0.0088	0.0350	0.0012
93	90	0.0300	0.0550	0.0018
121	125	0.0020	0.0197	0.00080
122	125	0.0077	0.0360	0.0015
123	125	0.0250	0.0590	0.0024

[a] The experimental errors for determining the product concentrations by quantitative gas chromatographic analysis were within 2% of measured concentrations.

Table X. Product Percentages from Reactions of the 2-Methallyloxyethyl Radical

Solution	Temp, °C	% Ia	% Ib	% Ic
41	40	16.0 ± 0.3	75.2 ± 1.5	1.75 ± 0.04
42	40	27.0 ± 0.5	64.6 ± 1.3	1.51 ± 0.03
43	40	40.1 ± 0.8	47.1 ± 1.0	1.10 ± 0.02
91	90	10.7 ± 0.2	80.2 ± 1.6	2.67 ± 0.06
92	90	17.7 ± 0.4	70.4 ± 1.4	2.41 ± 0.05
93	90	30.1 ± 0.6	55.1 ± 1.1	1.80 ± 0.04
121	125	8.1 ± 0.2	79.4 ± 1.6	3.22 ± 0.07
122	125	15.3 ± 0.3	71.7 ± 1.4	2.99 ± 0.06
123	125	24.8 ± 0.5	58.6 ± 1.2	2.38 ± 0.05

All solutions prepared in this manner are shown in Table VIII. Duplicate reactions were run to check the accuracy, and in each case both reaction mixtures showed the same product concentrations. The product concentrations and yield percentages from the reaction solutions listed in Table VII are given in Tables IX and X. The ratios of Ib to Ic at the various temperatures are shown in Table I.

Reactions of II and Bu_3SnH. The procedure from the preceding section for preparing the reaction solutions listed in Table IV for the 2-methyllyloxyethyl radical was again employed to prepare the reaction solutions for the 2-(2-phenylallyloxy)ethyl radical, which are described in Table XI.

The product analyses were carried out as before on a Hy-Fi Aerograph, using standard solutions of the authentic products to calibrate a 5-ft 30% SE-30 Column at 190 °C with the injection port at 290 °C. The product concentrations and yield percentages determined for the reaction solutions listed in Table XI are given in Tables XII and XIII. The ratios of IIc to IIb at the various temperatures are shown in Table II.

Reaction of 3-Phenyl-3-bromomethyltetrahydrofuran with Bu_3SnH. Again the same procedures for preparaing and analyzing the samples employed in the preceding experiments were used. A solution was prepared 0.1 M in Bu_3SnH, 0.1 M in 3-phenyl-3-bromomethyltetrahydrofuran, and 0.0017 M in AIBN. The degassed reaction tube was heated at 90 °C for 4 h and then analyzed. The only product of the reaction was 3-phenyl-3-methyltetrahydrofuran. No ethyl 2-phenylallyl ether or 3-phenyltetrahydropyran was observed.

Table XI. Reaction Solutions for Generation and Reactions of the 2-(2-Phenylallyloxy)ethyl Radical

Solution	Temp, °C	[Bu_3SnH]	[II]	[AIBN]
401	40	0.0261	0.0757	0.0004
402	40	0.0500	0.1490	0.0008
403	40	0.1023	0.3022	0.0015
901	90	0.0261	0.0757	0.0004
902	90	0.0500	0.1490	0.0008
903	90	0.1023	0.3022	0.0015
131	130	0.0250	0.0759	0.0004
132	130	0.0538	0.1505	0.0008
133	130	0.1000	0.3016	0.0017

Table XII. Product Concentrations from Reactions of the 2-(2-Phenylallyloxy)ethyl Radical[a]

Solution	Temp, °C	[IIa]	[IIb]	[IIc]
401	40	0.0021	0.0065	0.0119
402	40	0.0070	0.0114	0.0208
403	40	0.0242	0.0204	0.0370
901	90	0.0016	0.0066	0.0127
902	90	0.0055	0.0119	0.0228
903	90	0.0195	0.0213	0.0409
131	130	0.0012	0.0065	0.0129
132	130	0.0050	0.0125	0.0251
133	130	0.0155	0.0217	0.0433

[a] The experimental errors for determining the product concentrations by gas chromatography were within 2% of the measured concentrations.

Table XIII. Product Percentages from Reactions of the 2-(2-Phenylallyloxy)ethyl Radical

Solution	Temp, °C	% IIa	% IIb	% IIc
401	40	8.0 ± 0.2	24.9 ± 0.5	45.6 ± 0.9
402	40	14.0 ± 0.3	22.8 ± 0.5	41.6 ± 0.8
403	40	23.7 ± 0.5	19.9 ± 0.4	36.2 ± 0.7
901	90	6.1 ± 0.15	25.3 ± 0.5	48.7 ± 1.0
902	90	11.0 ± 0.2	23.8 ± 0.5	45.7 ± 0.9
903	90	19.1 ± 0.4	20.8 ± 0.4	40.0 ± 0.8
131	130	4.8 ± 0.10	26.0 ± 0.5	51.6 ± 1.0
132	130	9.3 ± 0.2	23.2 ± 0.5	46.7 ± 0.9
133	130	15.5 ± 0.3	21.7 ± 0.5	43.3 ± 0.9

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Nature of the Ortho Effect. Reactivity Correlations of the Acidic and Alkaline Hydrolyses of Ortho-Substituted *N*-Methylbenzohydroxamic Acids[1]

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Rates of acidic and alkaline hydrolyses of a series of ortho-substituted *N*-methylbenzohydroxamic acids have been determined at moderate acidity and very high basicity. The data are correlated by Taft's ortho polar and steric substituent constants. The results provide support for this method of correlation of quantitative data as well as support for the qualitative picture of ortho-substituent effects as described by McCoy and Riecke.

Introduction

The nature and quantitative treatment of the "ortho effect" has long interested chemists and is still unresolved.[2-4] The ratio of rate constants or equilibrium constants for similarly substituted *o*- and *p*-benzene systems[2] has been taken as a measure of ortho effects. Taft's separation of polar and steric ortho substituent effects is the best known treatment of ortho effects and has had some success in the correlation of data.[2,4] Equation 1 (Pavelich–Taft) quantitatively relates the log of the rate or equilibrium constants, k (k_0 is the constant for reaction of the compound with the reference substituent, methyl), to the polar (σ_0^*) and steric (E_s) substituent parameters for ortho-substituted benzene systems. ρ^* and δ are the respective reaction system susceptibility constants.

$$\log k = \rho^*\sigma_0^* + \delta E_s + \log k_0 \quad (1)$$

Charton has analyzed a large amount of data by linear regression and come to rather unconventional conclusions regarding the ortho effect,[2,5,6] e.g., that steric effects of ortho groups are minor. Charton represents Taft's steric effect substituent constant as

$$E_s = \alpha\sigma_I + \beta\sigma_R + \psi r_v + h \quad (2)$$

in which σ_I and σ_R are inductive and resonance substituent constants, respectively; r_v is related to the size of the substituent and is evaluated from van der Waals radii; h is an intercept term; α, β, and ψ are susceptibility constants. Charton considers the ψr_v term to be insignificant for ortho E_s values. The development and use of eq 2 and related equations has been criticized.[2,7]

McCoy and Riecke[8] have presented a qualitative picture of the ortho effect which reconciles the more conventional interpretations of proximity effects with those of Charton; in particular they have given a further interpretation to the h term of eq 2 and related equations. These authors consider and qualitatively analyze in some detail the effects of increasing the size of the ortho substituents. In the absence of specific interactions such as hydrogen bonding, the steric effect[8] will be composed of at least three effects: hindrance to solvation and to attack by a reagent, and steric hindrance to resonance. The first two effects will be rate reducing in typical ester reactions, e.g., those used by Taft to define σ^* and E_s, while the last will be a rate enhancing factor—the conjugation of the carbonyl group with the aromatic ring will be reduced in the reactant state compared to a nonhindered substrate, and in either case, the conjugation should be stronger in the

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