Radical Production from the Interaction of Closed-Shell Molecules. 10. Chemistry of Methylenecyclohexadiene and the Thermal Polymerization of Styrene[1e]

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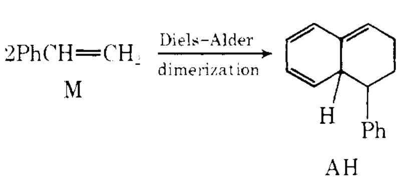
Pyrolysis of 5-methylenebicyclo[2.2.1]hept-2-en-7-one produces 5-methylene-1,3-cyclohexadiene (MCH). We have studied MCH as a model for the Diels–Alder dimer of styrene (AH). The styrene dimer is postulated to be involved in radical production, by a molecule-assisted homolysis (MAH) process, in the spontaneous polymerization of styrene. Surprisingly, however, no increase in the rate of polymerization of styrene is observed upon addition of MCH, even though MCH reacts rapidly with styrene to give ene products. The rate of radical production from the reaction of styrene with MCH must be at least 20 times slower than that attributed to AH and styrene. A detailed analysis is presented of the fractions of AH and MCH that undergo the various reactions open to these reactive species: initiation, chain transfer, and ene reaction. Surprisingly, <2% of the AH undergoes the MAH reaction; however, this process can be detected since it leads to the formation of long-chain polymer molecules. The fraction of AH that undergoes chain transfer also is very small, despite the large transfer constant. Most of the AH reacts with styrene to give trimeric products, probably both by an ene process and by cage radical recombination. The situation is similar for MCH, except that the fraction undergoing the MAH initiation is even smaller or is zero. Data are also presented on the time for AH to reach its steady state level in styrene at 60 °C, judged from the UV absorbance at 320 nm. It is argued that an induction period should be observed in the rate of thermal polymerization if the Diels–Alder MAH initiation mechanism is correct. However, no induction period has been reported at 60 °C. A rationalization is presented that attempts to explain the different rates of radical production from ene reactions and/or MAH processes from MCH and AH. The apparent faster rate of MAH initiation by AH relative to MCH can be rationalized by postulating a more open transition state in an ene-like reaction caused by steric effects for AH or to other differences between the MCH- and the AH-styrene reactions. Alternatively, however, it is argued that our results may require rejection or modification of the proposed MAH reaction of AH as the initiation step in the polymerization of styrene. The transfer constant of MCH is the largest ever reported for a hydrocarbon, and indeed one of the largest on record, about 9 at 60 °C in styrene.

For some time we have been interested in the processes by which closed-shell, stable molecules interact to produce free radicals.[1] One mechanism by which this can occur, molecule-assisted homolysis (MAH), can be formulated as in eq 1, where the homolysis of the A–B bond is assisted by some type of bond-formation process with molecule C.[1a,g]

$$\mathrm{A{-}B + C \rightarrow A\cdot + BC\cdot} \qquad (1)$$

A large body of evidence points to an MAH process as being involved in the self-initiated polymerization of styrene.[1,2] The interaction of a styrene monomer molecule (M) with the styrene Diels–Alder dimer (AH, see eq 2) is postulated to involve the transfer of a hydrogen atom as shown in eq 3.



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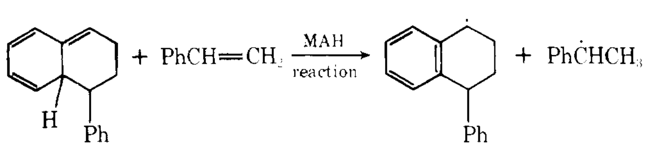

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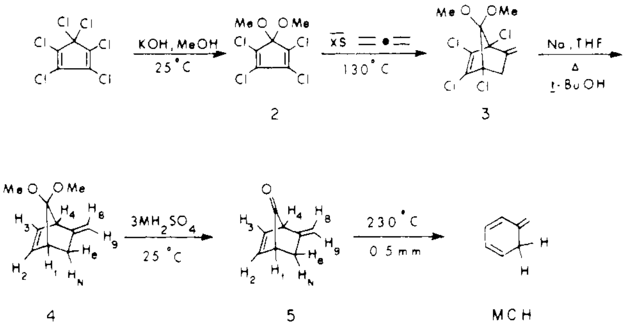
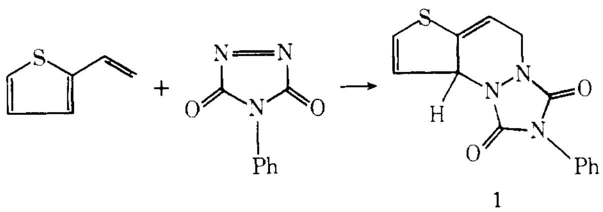
The Diels–Alder dimer of styrene has never been isolated; however, several of its oxidized and aromatized derivatives have been reported.[1g,2b] In addition, models of the styrene dimer have been synthesized and tested as possible MAH initiators. For example, we have synthesized the heterocyclic compound (1) shown in eq 4, and it appears to initiate the polymerization of styrene.[1d]

Scheme I





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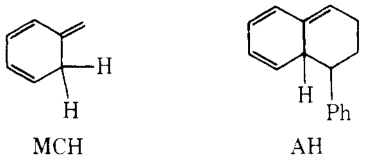
We here report a study of 5-methylene-1,3-cyclohexadiene (MCH) as a model for the styrene Diels–Alder adduct (AH);



MCH AH

the close structural similarities between MCH and the styrene dimer are obvious. Although MCH was synthesized some time ago,[3] the literature synthesis required laborious, repetitive gas chromatography (GLC) to isolate the quantities of MCH we needed. Therefore, we have developed the improved synthesis outlined in Scheme I. The pyrolysis of ketone 5 was done on

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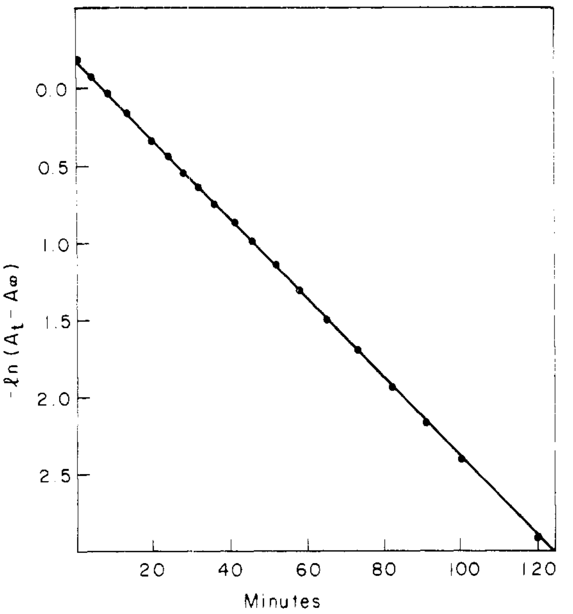


Figure 1. First-order plot of change in absorbance at 350 nm of a 2.5 × 10^{-3} M solution of 5-methylene-1,3-cyclohexadiene (MCH) in 8.35 M styrene at 60 °C.

Table I. Observed Pseudounimolecular Rate Constants for the Decay of 5-Methylene-1,3-cyclohexadiene (MCH) in 8.35 M Styrene at 60 °C

[MCH][a] × 10^3, M	k_{dis} × 10^4, s^{-1}	$t_{1/2}$, min	wavelength used, nm
0.37[b]	4.3	27	315
0.37[b]	3.5	33	330
0.37	3.2	36	343
0.39[b]	4.5	26	315
0.39[b]	3.7	31	330
0.39	3.8	30	343
2.31	3.4	34	350
2.54	3.6	32	350
10.96	4.1	28	360
13.59	3.6	32	360
17.00	4.1	28	370
av:	3.8 ± 0.4	31 ± 3	

[a] Concentration was determined from initial absorbance using the extinction coefficients in Table VI. [b] Concentration was determined from absorbance at 343 nm.

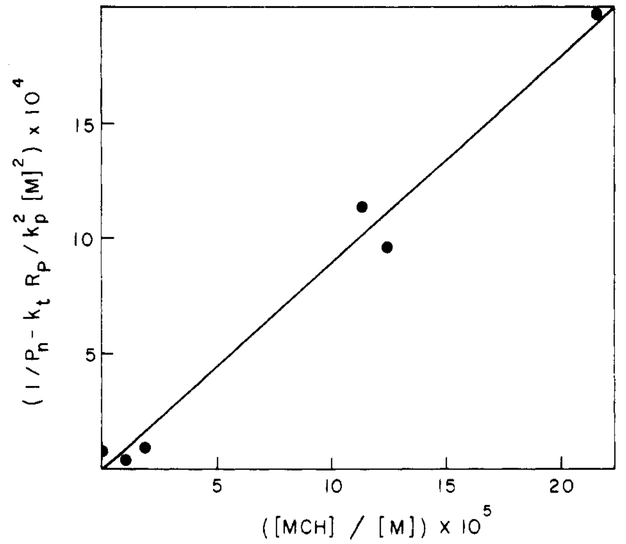


Figure 2. Determination of transfer constant of 5-methylene-1,3-cyclohexadiene (MCH) from degree of polymerization ($\overline{P}_n$) of styrene, where $1/\overline{P}_n = (k_t R_P/k_p{}^2[M]^2) + C([MCH]/[M])$ and R_P is held constant using AIBN (see Experimental Section). The value of C obtained from the slope is 9.1 at 60 °C.

Table II. Observed Rates of Polymerization at 60 °C of 8.35 M Styrene with Added 5-Methylene-1,3-cyclohexadiene (MCH)

[MCH] × 10^2, M	R_P × 10^6,[a] M s^{-1}	conversion,[b] %
0.00	2.06[c]	
0.00	1.98	0.39
0.04	1.99	1.26
0.12	1.43	0.64
0.27	2.09	2.13
1.17	1.81	0.16
1.53	1.25	0.11

[a] R_P (M s^{-1}) = % conversion × 8.35/t (s) × 10^2. [b] Determined gravimetrically. [c] Cf. ref 13.

neat material, and the subsequent GLC purification gives comparatively large samples of MCH.

Results and Discussion

Synthesis of 5-Methylene-1,3-cyclohexadiene (MCH). A synthesis of MCH was reported in 1962 by Bailey and Baylouny,[3] and recently Kopecky and Lau[4] have reported an alternative route. In preliminary work, we found that the Bailey synthesis could not provide sufficient material of the requisite purity for our purposes, and since the Kopecky method involves an electrolysis that appeared troublesome, we have developed a third synthesis that we believe is the most trouble-free of the three and is capable of yielding concentrated MCH solutions.

Our method is outlined in Scheme I. It involves the preparation of the ketone **5**, which is decarbonylated to give MCH. This gives a fivefold increase in MCH yield relative to the corresponding step in Bailey's method. The details of our synthesis are given in the Experimental Section.

Disappearance of 5-Methylene-1,3-cyclohexadiene (MCH) in Styrene. As shown in Figure 1, the disappearance of methylenecyclohexadiene (MCH) in styrene at 60 °C (followed by UV) is pseudounimolecular in MCH with a half-life, independent of concentration, of about 31 min (see Table I). Although MCH reacts rapidly in styrene solution, there is, surprisingly, no significant change in the rate of polymerization of styrene with 0.001–0.01 M added MCH (Table II).

However, MCH does produce a large effect on the molecular weight of the polystyrene formed in its presence (see Figure 2). Clearly, therefore, MCH is a remarkably reactive chain transfer agent that transfers a methylene hydrogen to a polystyryl radical in a fast reaction (eq 5). However, like most

$$M_n\cdot + MCH \xrightarrow{k_{tr}} \text{polymer} + PhCH_2\cdot \qquad (5)$$

transfer agents in styrene, MCH does not affect the rate of polymerization to a significant extent. As indicated in Figure 2, the chain transfer constant ($C_{MCH} = k_{tr}/k_p$) of MCH is 9.1 at 60 °C, the largest transfer constant reported for any hydrocarbon. In fact, MCH ranks with thiols and is among the best transfer agents known.

Decomposition of MCH in Other Solvents. It has been reported that the isomerization of MCH to toluene is slow in the absence of mineral or organic acids.[3,5] However, since isomerization might compete with the molecule-assisted homolysis reaction in styrene, we explored the reactivity of MCH in various solvents to obtain a bench mark for our subsequent studies in styrene.

Table III. Observed Second-Order Rate Constants for the Decay of UV Absorbance of 5-Methylene-1,3-cyclohexadiene (MCH)[a]

[MCH] $\times 10^4$, M	temp, °C	$k_{dis} \times 10^2$, $M^{-1} s^{-1}$	solvent
3.77	24	13.3	octane[b]
3.36	40.2	2.52	octane[c]
3.86	40.2	24.9	octane[c]
3.00	60.5	27.1	decane[b]
3.53	60.5	4.2	decane[d]
5.68	60.5	18.2	decane[d]
4	60.5	>1000	chloroform[d]
9.70	60.5	0.26	benzene[d]
9.20	80	0.86	benzene[d]
9.70	80	28.5	benzene[d]

[a] In octane, decane, and chloroform at 303 nm and in benzene at 343 nm. [b] No degassing. [c] Degassed by flushing with argon for 3 min. [d] Vacuum degassed.

We followed the disappearance of MCH using its UV absorbance at various wavelengths from 315 to 370 nm. As indicated in Table III, the precision of the rate constants is poor. We feel that this probably is due to catalysis by adventitious impurities or by the glass walls of the UV cells, since variations in rate occur even among samples vacuum-transferred simultaneously from the same bulk solution and degassed and sealed in identical manner. In spite of this problem with precision, a large solvent effect is obvious. For example, the rate of disappearance of MCH in chloroform is much faster than in benzene. While the disappearance of MCH in decane or octane is faster than in benzene, it is still slower than in chloroform. The kinetics in decane or benzene are second order in MCH (Figure 3), and the major product, analyzed by GLC or NMR (in benzene-d_6), is toluene. In the presence of oxygen, the product in chloroform is benzyl hydroperoxide.[6]

Second-order kinetics suggest that a chain process, radical or ionic, may be involved in the conversion of MCH to toluene. The question of whether MCH undergoes an unassisted, nonchain unimolecular rearrangement to toluene is of considerable interest. Preliminary studies with hydroquinone indicate that the reaction is slower in the presence of this inhibitor, but again the rates were not reproducible. It would be desirable to have an inhibitor that entirely stopped any radical chain decomposition process, but it is obvious that such an inhibitor will be very difficult to find for the super-reactive MCH. Stable radicals such as DPPH and galvinoxyl abstract hydrogen from MCH, and even inhibitors such as styrene cannot be used. Thus, it probably will be necessary to study the possible unimolecular rearrangement of MCH in the vapor phase.

In any case, the data of Table III show that the rate of decay of MCH in benzene or decane at 60 °C is at least a factor of ten lower than the rate in styrene (Table I). Therefore, the conversion of MCH directly to toluene probably is not important during the polymerization experiments reported here.

Thermal Polymerization of Styrene. The proposed mechanism for the self-initiated polymerization of styrene that has gained the largest acceptance[1g,2] is that, suggested originally by Mayo,[2a] involving an MAH reaction by the Diels–Alder dimer as the critical initiation step (eq 3). In view of the considerable structural similarity between MCH and the styrene dimer, we find it surprising that MCH does not initiate the polymerization of styrene. The comparison between the styrene dimer and MCH can be clarified by a numerical analysis of the fraction of each of these reactive molecules that undergoes the various reactions possible: MAH initiation, chain transfer, and ene reaction with styrene.

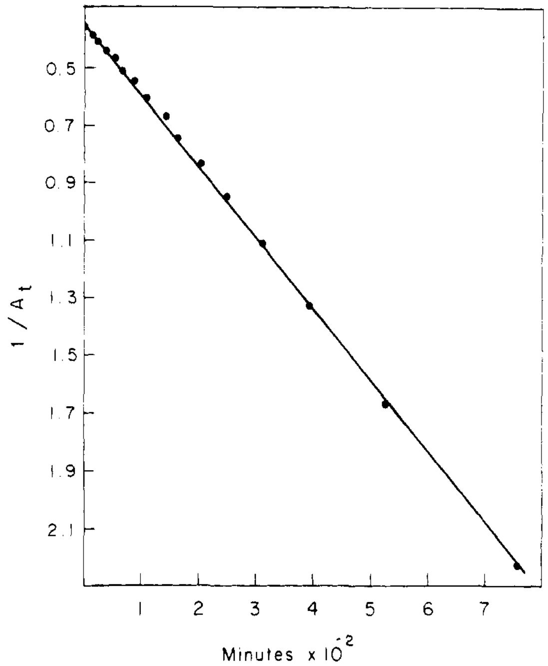


Figure 3. Second-order plot of change in absorbance at 303 nm of a 6.3×10^{-4} M solution of 5-methylene-1,3-cyclohexadiene (MCH) in decane at 60.5 °C.

Identification of AH in Styrene. Pryor and Patsiga,[7] and more recently Buchholz and Kirchner,[8] have noted that the Diels–Alder dimer (AH) should have an absorption at about 320 nm[9] that should be detectable in neat styrene. By following the appearance of this absorbance, the rate of appearance of AH at various temperatures can be inferred. The analysis of Buchholz and Kirchner[8] at 64 °C gives the rate of dimerization of styrene (R_D) as 4.9×10^{-9} M s^{-1} and the rate constant (k_D) as 7×10^{-11} M^{-1} s^{-1}; the rate constant for trimerization (k_T) is 8.5×10^{-6} M^{-1} s^{-1} (see eq 6a and 6b).

$$2M \xrightarrow{k_D} \text{styrene Diels–Alder dimer (AH)} \tag{6a}$$

$$AH + M \xrightarrow{k_T} \text{trimer} \tag{6b}$$

The UV absorbance indicates that AH reaches its steady state concentration (6.5×10^{-5} M) only after purified styrene[10] is heated for more than 9 h at 64 °C. These rate constants along with our results and those of others enable one to analyze rather fully the competing reactions of AH in styrene.

Products from AH in Styrene. It should first be noted that nearly all (94%) of the AH produced in styrene at 64 °C ends up as trimeric product. This has been stressed before and discussed in the context of the MAH mechanism.[2b,11]

The rate of initiation of polymerization by an initiator I is defined by eq 7,[12] where f is the fraction of I which initiates

$$R_i = 2k_t R_P^2 / k_p^2 [M]^2 = 2fk_d[I] \tag{7}$$

polymerization. Using the accepted values at 60 °C for the rate of thermal polymerization of styrene ($R_P = 2.06 \times 10^{-6}$ M s^{-1}),[13] $k_t/k_p^2 = 861$,[14] and monomer concentration ([M] = 8.35 M),[15] the rate of thermal initiation can be calculated to be 1.0×10^{-10} M s^{-1}. The rate of formation of AH, calculated above for eq 6a, is 4.9×10^{-9} M s^{-1}. If steady state conditions (eq 8)

$$d[AH]/dt = 0 = k_D[M]^2 - R_{dis} \tag{8}$$

are met, then the rate of formation of AH must be equal to the rate of its disappearance by all routes, here defined as R_{dis}. The fraction (f) of the styrene dimer that reacts to produce

Table IV. Comparison of the Reactions of the Styrene Diels–Alder Dimer (AH) and 5-Methylene-1,3-cyclohexadiene (MCH) in Styrene at 60 °C[a]

compd I	disappearance total rate[b]	trimerization		transfer		assisted homolysis	
		rate[c]	% of total	rate[d]	% of total	rate[e]	% of total
AH	0.49×10^{-8}	0.46×10^{-8}	94	1.4×10^{-10}	2.8[f]	53×10^{-12}	1.1
MCH	2.5×10^{-8}	2.2×10^{-8}	90[g]	1.5×10^{-10}	0.6	0.25×10^{-12}	0.001[h]

[a] Showing the percent reaction of the compounds by each pathway. [b] In M s^{-1}; $R_{dis} = k_{dis}[I] = k_D[M]^2$ (eq 8). AH is assumed present at its steady state level (6.5×10^{-5} M) throughout; MCH is initially present at 0.01 M (the highest concentration we studied) and disappears at a rate calculated by point-to-point integration. [c] In M s^{-1}; $R_T = k_T[I][M]$ (eq 6b for AH, eq 9 for MCH). [d] In M s^{-1}; (eq 5) $R_{tr} = k_{tr}[I][M_n\cdot] = CR_P[I]/[M]$. [e] In M s^{-1}; $R_{MAH} = 0.5R_i$ (eq 7). [f] Value of C_{AH} was taken as 8.5; see text and ref 26. [g] Reference 4. [h] Upper limit, assuming a factor of 2 as the experimentally observable lower limit of detection of a change in the rate of polymerization.

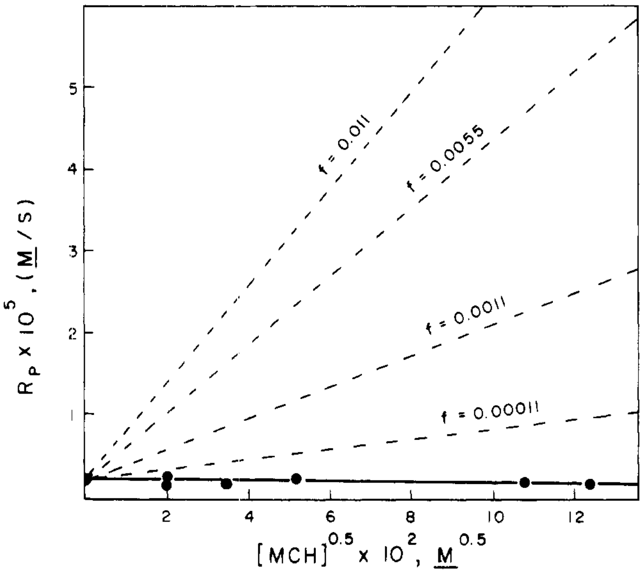


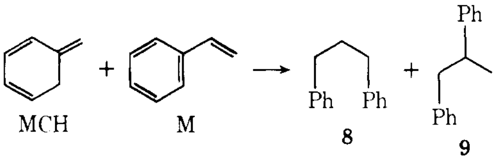
Figure 4. Rates of styrene polymerization with added 5-methylene-1,3-cyclohexadiene (MCH): solid line, experimentally observed rates from Table II; broken lines, rates projected, assuming various efficiencies of initiation (f) (eq 7).

radicals is then $R_{i,th}/2R_{dis}$, or 0.011. Thus, nearly 99% of the AH in styrene reacts by routes that do not give scavengable radicals.

The chain transfer constant of AH has been calculated to be 1.[16] This value is large, but not surprising when compared to that determined for MCH. However, despite this large transfer constant, only about 3% of AH disappears by transfer.

Table IV summarizes the relative importance of the various modes of reaction of the Diels–Alder dimer (AH) in styrene. The total rate of disappearance (R_{dis}) of the dimer is derived from steady state conditions (eq 8) as indicated above. The rate of trimerization (R_T), calculated from Buchholz and Kirchner's[8] rate constants and the steady state concentration of AH, is 94% of the total rate of disappearance. The rate of chain transfer (R_{tr}), calculated from the chain transfer constant, is found to represent only about 3% of the total rate even though the transfer constant is very large. The last column in Table IV, the rate of the postulated molecule-assisted homolysis reaction (R_{MAH}), calculated as indicated above, accounts for the disappearance of only about 1% of the AH present. Clearly, trimerization and transfer consume the largest portion of the styrene dimer, and the proposed MAH initiation step is only a very minor mode of reaction.

Products from MCH in Styrene. A similar analysis can be made for MCH. Although MCH does not initiate the polymerization of styrene, Kopecky and Lau[4] have reported that MCH reacts nearly quantitatively by an ene reaction[17] with styrene. The products, 1,3- and 1,2-diphenylpropane (eq 9), correspond mechanistically to the styrene trimer (eq 6b).



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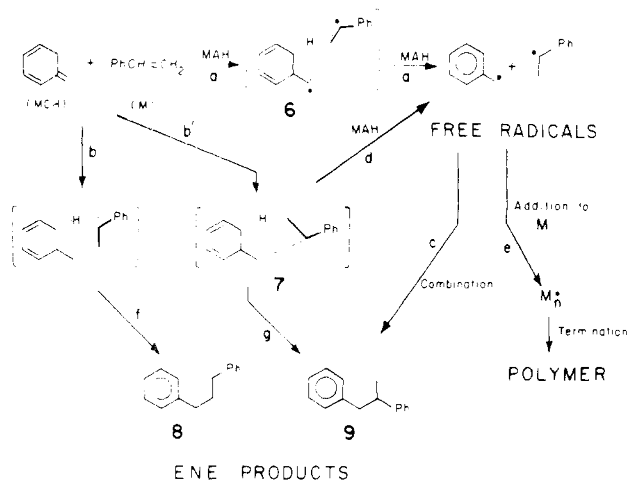
Chain transfer is, of course, another route by which MCH disappears. However, in spite of the extremely large transfer constant, transfer again is found not to be very important when compared to addition of MCH to styrene to give 8 and 9.

MCH as a Model. The data in Table IV allow a comparison to be made of the relative importance of the modes of reaction of MCH and the styrene dimer in styrene at 60 °C. As can be seen in the first column, MCH is six times more reactive overall than AH. Trimerization (eq 9 for MCH) consumes the largest portion of the MCH present, as it does in the case of AH. Since the transfer constants of MCH and AH are nearly the same, the percentage of transfer in the case of MCH is again very small in spite of the large transfer constant. In the last column we have calculated an *upper limit* for the molecule-assisted homolysis reaction of MCH as described below.

The marked inability of methylenecyclohexadiene (MCH) to model the initiation attributed to the styrene dimer (AH) is represented graphically in Figure 4. The lower, solid line represents the experimentally observed rates of polymerization. We have also calculated the *expected* rates of polymerization initiated by MCH present using the observed rate constant for the disappearance of MCH in styrene ($k_{dis} = 4 \times 10^{-4}$ s^{-1}, Table I) and assuming various values for the efficiency (f). If the efficiency of radical production by MCH were the same as that for AH (0.011), then the upper, broken line of Figure 4 is obtained. If this efficiency were correct, even at the smallest concentration of MCH used experimentally (4×10^{-4} M), the rate of polymerization should be 1.4×10^{-5} M s^{-1}, seven times faster than that for pure styrene. We have actually studied concentrations of MCH as high as 1.53×10^{-2} M, and if we conservatively estimate our limit of detection of a change in the rate of polymerization as a factor of 2, then MCH can have a value of f no larger than 0.00001, a factor of 10^{-3} smaller than that of AH (see Table IV). Clearly, then, if we assume that styrene's dimer (AH) is indeed involved in styrene polymerization other than as a chain transfer agent, MCH is a surprisingly poor model for AH.[18]

MAH Transition State. Scheme II outlines possible reactions of MCH (or AH) in styrene. The 1,3-diphenylpropane (8) produced can best be rationalized by reactions b and f of Scheme II. Product 9 could arise from analogous processes (b′ and g); however, since the parallel reactions of AH and related species[1d] seem to lead to scavengable free radicals, product 9 might arise from reactions a and c or b′–d–c as well.

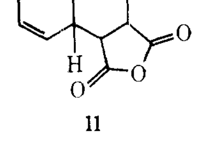
Scheme II



Two distinct types of transition states for the molecule-assisted homolysis reaction of MCH (or AH) can be considered. The first is a cyclic, ene-like[17] transition state (7) that can give scavengable radicals via reaction d, Scheme II. (Indeed some ene reactions appear to involve free radicals since they are sensitive to free radical initiators and inhibitors.[20]) The second MAH transition state could involve an open, extended conformation in which the radical centers are formed far apart (6). Radicals formed in this process may combine to form ene-type products (reaction c) (trimer for AH and diphenylpropane for MCH) or diffuse apart (reaction e) and initiate polymerization.

This speculation on the mechanism of the ene reaction suggests a possible rationale for the apparent larger yield of radicals from AH–styrene than from MCH–styrene reactions. The ene reaction is known to be very sensitive to steric effects,[21a] and models indicate that the repulsive interactions in 7 for the AH–styrene transition state may be greater than those in the MCH–styrene reaction.[21b] In addition, it should be noted that the postulated MAH steps involve donation of a more labile *tertiary* hydrogen from AH to give a *secondary* benzylic radical, whereas MCH would be required to donate a *secondary* hydrogen to give a *primary* benzylic radical. These effects together may allow AH–styrene to adopt an extended transition state analogous to 6, or to have more radical character in a transition state analogous to 7 and thus a greater yield of radicals via reaction d. That is, the AH–styrene ene reaction may "leak" a small fraction of free radicals, whereas the MCH–styrene reaction may be more nearly concerted and simultaneous.

Model Compounds. The evidence is convincing that the styrene Diels–Alder dimer (AH) is produced. Isolation of molecules containing the phenyltetralin moiety,[2b,22] the observation of UV absorbances in the proper wavelength regions,[7-9] and the high molecular weights observed at short times[1b,g] (see below) are difficult to rationalize otherwise. However, evidence implicating AH in the generation of radicals clearly is far less conclusive. The results of attempts to model the reactivity of AH are surprisingly discouraging. Table V shows several compounds that have been studied. The experiments with 1 and 10 in styrene and methyl acrylate[1d] and 11 with methyl methacrylate[23] support the proposed MAH reaction of AH and styrene. However, MCH appears intuitively to be a much better model for AH than are 1, 10, or 11. Therefore, our results, as well as the independent study of Kopecky and Lau[4] on MCH, raise disturbing questions about the ability of AH to undergo eq 3.



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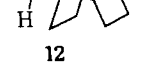

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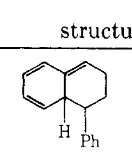
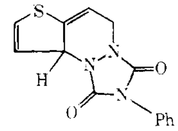
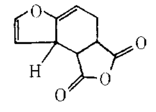
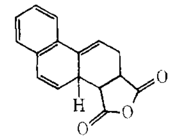
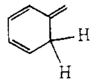
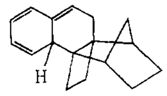
Table V. Initiating Ability of Synthetic Model Compounds of the Proposed Styrene Diels–Alder Dimer (AH)

model	structure	ability to initiate?	monomer used for test
AH		?	styrene
1		yes[a]	styrene, methyl acrylate
10		yes[a]	styrene
11		yes[b]	methyl methacrylate
MCH		no[c]	styrene, methyl acrylate
12		no[d]	styrene

[a] Reference 1d. [b] Reference 23. [c] This work and ref 4. [d] Reference 24.

Compound 12 also has been reported not to affect the rate of polymerization of styrene.[24] If, as suggested above, steric factors are the cause of the differences between the ability of AH and MCH to initiate polymerization, then it is especially difficult to explain the lack of activity of compound 12. The open MAH transition state (6) should be even more favored over the closed ene-like configuration for 12 than for AH. One would expect 12 to be an even better initiator than AH.

Other Problems with the MAH Mechanism. Aside from the problem of determining how well the model compounds mimic the properties of AH, Pryor and Patsiga's[7] and Buchholz and Kirchner's[8] observations of the long period of time necessary before a steady state of AH is reached raise problems. If the 320–340 nm absorbance is due to AH, then the rate of polymerization at 60 °C should be initially zero and increase over a 9-h period before leveling off at the plateau value observed after AH reaches its steady state concentration. No such effect has been observed at 60 °C, although a 1-h induction period at 30 °C has been reported.[25b,d]

Despite this failure to observe substantial induction periods in the rate of thermal polymerization of styrene, an induction period can easily be observed in the chain transfer activity as AH builds up to its plateau concentration. At very low conversions (0.01%), the polymer molecular weights are far in excess of that observed at higher conversions[25] and the limiting molecular weight is attained only after several hours. This observed anomaly is qualitatively consistent with a detectibly slow build up of the dimer (AH), a very efficient transfer agent.

Expected Change in $\overline{P}_n$ and R_P with Time. These speculations on the polymer molecular weight, $\overline{P}_n$, and the rate of polymerization (R_P) at short times can be put on a

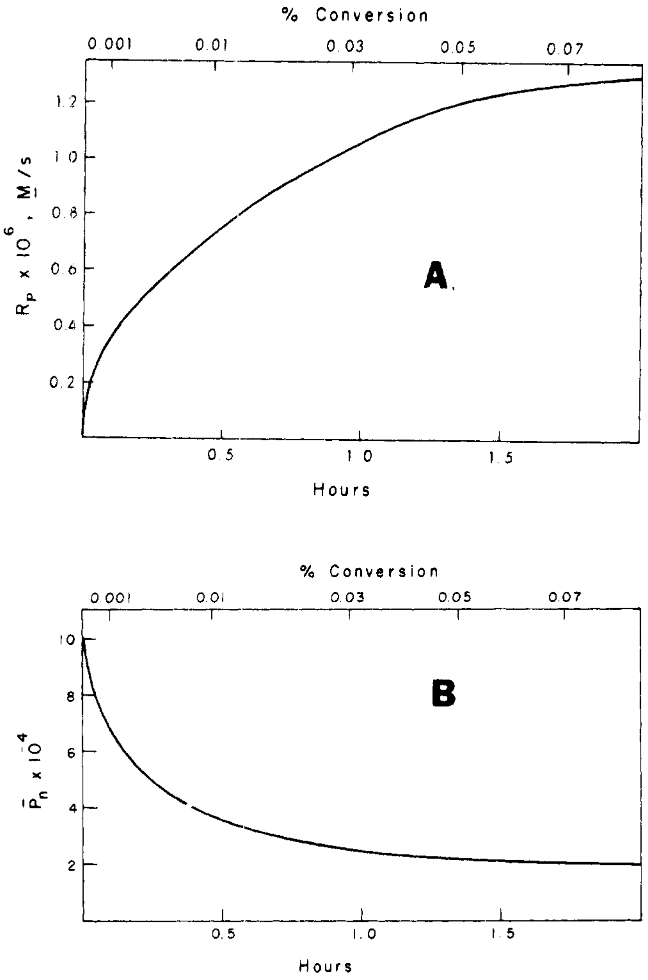


Figure 5. (a) Rate of styrene polymerization (R_P) as a function of time calculated from eq 7 assuming initiation is due only to the interaction of the styrene dimer (AH) and styrene. The concentration of AH at any time is determined from the data of Buchholz and Kirchner;[8] at times less than 1 h, it is assumed that [AH] = $1.72 \times 10^{-5} \times$ time (h). (b) Number average degree of polymerization ($\bar{P}_n$) as a function of time calculated from eq 10, using the results in Figure 5a and assuming that transfer occurs only to styrene monomer or styrene dimer (AH).

quantitative basis. We have performed such a calculation, and the results are surprising.

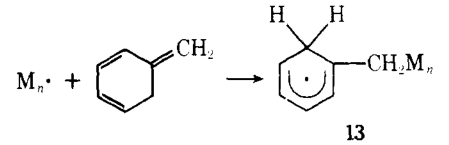
Equation 10 defines the number average degree of polymerization ($\bar{P}_n$) in terms of the rate of polymerization and the chain transfer constants of monomer (M) and dimer (AH).[1a] At low conversions, high molecular weight polymer is formed since transfer occurs predominantly to monomer, which has a very small transfer constant (C_M). As the Diels-Alder dimer (AH) reaches its steady state concentration, it becomes the principle transfer agent and $\bar{P}_n$ reaches its plateau value.

$$1/\bar{P}_n = (k_t R_P/k_p^2[M]^2) + C_M + C_{AH}([AH]/[M]) \quad (10)$$

Figures 5a and 5b illustrate the changes in R_P and $\bar{P}_n$ at 60 °C based on eq 7 and 10, using the values calculated[26] for the transfer constants of styrene monomer and dimer and the observed time dependence for the buildup of AH. (These calculations assume that initiation is due only to the interaction of AH and styrene, and that AH and monomer are the only transfer agents present.) The instantaneous rate of polymerization calculated at the end of 2 h is 1.3×10^{-6} M s^{-1}, only 60% of the reported rate;[13] the average over 2 h is about 1.0×10^{-6} M s^{-1}, less than half the literature value. Such differences would appear to be easily detected experimentally, but have not been reported.

In contrast, plots of UV absorbance[7,8] and polymer molecular weight[25h] vs. time suggest that the styrene Diels-Alder dimer reaches its steady state concentration so slowly that induction periods should be observed in thermal polymerizations at 60 °C (for example, see Figure 5b). The fact that no induction period has been reported at 60 °C again raises disturbing questions for the Diels-Alder MAH mechanism.

Transfer Reaction of MCH and AH. These two molecules have the largest chain transfer constants for any hydrocarbon reported. Their surprisingly large reactivity is clear, for example, when it is realized that triphenylmethane has a transfer constant in styrene at 60 °C that is 10^5 smaller than either AH or MCH. A possible rationale for the large transfer constant of these molecules, despite the absence of discernible MAH activity in the case of MCH, is that transfer involves initial *addition* of the polymeric radical to the transfer agent (eq 11)



13

(11)

rather than abstraction of the labile hydrogen (eq 5). The subsequent hydrogen donation from **13** then involves the simultaneous aromatization of the ring (eq 12). Radical **13** also

$$13 + M \rightarrow PhCH_2M_n + HM\cdot \quad (12)$$

$$13 + M_n\cdot \rightarrow PhCH_2M_n + HM_n \quad (13)$$

would be expected to disproportionate and combine with the polymeric radical (eq 13), making MCH a retarder and giving degradative transfer. This is not observed; however, the rate of eq 12 may well be greater than that of eq 13.

Conclusions

The question of the source of the radicals that are responsible for the spontaneous polymerization of styrene has generated considerable controversy, and several mechanisms have been proposed. The mechanism involving the Diels-Alder dimer (AH) has been widely accepted and is supported by a variety of types of experimental work.[2] However, the ineffectiveness of some models of AH to initiate styrene is very difficult to rationalize. The compounds that appear to be the best models, 5-methylene-1,3-cyclohexadiene (MCH) and compound **12**, do not initiate, while **1**, **10**, and **11** appear to initiate and lend support to the AH mechanism (see Table V).

All of these compounds have labile hydrogens and may readily undergo air oxidation. Indeed, our early studies of MCH gave spuriously high polymerization rates due to the very facile and solvent dependent oxidation of MCH to benzyl hydroperoxide.[6] This hydroperoxide, of course, does initiate styrene's polymerization. Although in the case of **1** the hydroperoxide as a potential impurity was considered and discounted,[1d] the possibility of an initiating impurity being present cannot be totally ruled out.

At this time, two viewpoints can be argued. The first and most conservative accepts the Diels-Alder MAH mechanism as correct for styrene. It requires that MCH (as well as compound **12**) be regarded as a poor model for AH (because of the ene reaction argument given above or for some other reason). It also requires either that Buchholz and Kirchner's[8] and Pryor and Patsiga's[7] data on the time necessary for the buildup of the styrene dimer are incorrect or that there actually is a measurable induction period in styrene's thermal polymerization. (The data on the buildup of dimer are based on UV absorbance, and other oligomers could be responsible for the absorbance observed, although the structure of other compounds that would absorb at 320–340 nm is not at all obvious.[9,10] It also is possible, although an induction period in thermal polymerization has not yet been reported at 60 or 100 °C, that an induction period will be found if well-designed experiments are performed, and we are beginning such experiments.)

A second and less conservative possibility is that the Diels–Alder MAH mechanism for the initiation of styrene is wrong. One difficulty with this conclusion is that evidence of many types has been interpreted as supporting the MAH mechanism.[2b,28] However, as we have said,[1g,2b] most of this evidence (e.g., molecular weight and UV absorbance at low conversions[28]) merely proves that AH is *present* and is an excellent transfer agent, but does not establish the occurrence of eq 3. Another difficulty is that there are very few viable alternatives to the AH mechanism. A diradical–transfer mechanism[1c] has been suggested for some monomers such as pentafluorostyrene and methyl methacrylate that appear unlikely to undergo the Diels-Alder MAH mechanism, but the diradical mechanism also has difficulties.[1c] Clearly, the critical experiment is the synthesis and testing of AH itself as an initiator, and we hope to do this using a scheme like that used to prepare MCH.

Experimental Section

General. Commercial styrene was purified by three extractions with 10% NaOH to remove inhibitor followed by washing with water and drying over anhydrous Na_2SO_4. The styrene was filtered through alumina and then fractionally distilled at reduced pressure (bp 70 °C at 22 mmHg). It was stored at 0 °C and vacuum-transferred or distilled again just before use.[10] Octane, decane, and benzene were washed with concentrated H_2SO_4 and HNO_3 and then with water, dried over Na_2SO_4, and then distilled from sodium. Chloroform was washed with water, dried, and distilled from $CaCl_2$.

NMR spectra were run on a Varian A-60 or HA-100 spectrometer using tetramethylsilane as an internal standard. IR spectra were recorded from thin film samples on a Perkin-Elmer Infracord.

Gas chromatographic analyses and purifications were carried out on a Varian-920 instrument equipped with a thermal conductivity detector and operated with He as carrier gas.

Synthesis of 5-Methylene-1,3-cyclohexadiene (MCH). A. The procedure of Bailey and Baylouny[3] was followed, and the dilute pentane solution of MCH obtained was purified by GLC on a 1.5 × 3.5 mm i.d., 10% OV-101 column operated at 35 °C with an injector and detector temperature of 100 °C and a helium carrier gas flow of 20 mL/min. The ratio of toluene/MCH was never greater than 1. Due to the large size of the samples injected (300 μL), retention times of 60–70 min were necessary to gain separation of MCH and toluene due to column overloading. Usually four injections were required to give 1 mg of MCH. This method proved unsatisfactory for the large samples we required.

B. 1,2,3,4-Tetrachloro-5,5-dimethoxycyclopentadiene (2).[29] A solution of hexachlorocyclopentadiene (50.8 g, 0.186 mol) in 160 mL of methanol was placed into a three-neck round-bottom flask fitted with a condenser, mechanical stirrer, and addition funnel. Over a period of 1.5 h, a solution of potassium hydroxide (24.9 g, 0.44 mol) in 120 mL of methanol was added via the addition funnel to the stirred solution. The resulting mixture was stirred for 3 h. The reaction mixture was poured onto 600 g of ice. After the ice melted, the aqueous mixture was extracted with four 50-mL portions of methylene chloride. The extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated under vacuum. The product distilled at 59–61 °C (0.5 torr).

7,7-Dimethoxy-1,2,3,4-tetrachloro-5-methylenebicyclo-[2.2.1]hept-2-ene (3).[30] A stainless steel bomb was charged with 2 (10 g, 38 mmol) and allene (30 g, 0.75 mol). The bomb was heated in an oil bath regulated at 130 °C for 16 h. After recovering the excess allene, the crude product was distilled. The product distilled at 83–84 °C (0.1 torr) to give a center fraction of 6.3 g (55%). The ^1H NMR spectrum agreed with reported values.[30]

7,7-Dimethoxy-5-methylenebicyclo[2.2.1]hept-2-ene (4).[29] A solution of **3** (28.0 g, 0.092 mol) was added over 2 h to a refluxing mixture of sodium cubes (30.0 g, 1.3 mol), 300 mL of dry tetrahydrofuran, and 38 mL of dry *tert*-butyl alcohol in a three-neck round-bottom flask. The resulting dark solution was refluxed for 17 h. After filtering off the excess sodium, the solution was poured into a mixture of ether and ice. The organic layer was washed with saturated aqueous sodium chloride solution until the washings were only slightly colored. The ethereal solution was dried over anhydrous magnesium sulfate and filtered, and the solvent was removed under vacuum. The product was bulb-to-bulb distilled. The ketal **4** was collected at about 100 °C (20 torr), giving 4.8 g (31%): ^1H NMR (CCl_4)[31] δ 1.63 (H_n, dt, $J_{n,e}$ = 14 Hz, $J_{n;8,9} \simeq 2$ Hz), 2.46 (H_e, dp, $J_{e,n}$ = 14 Hz, $J_{e;1,8,9} \simeq 2$ Hz), 2.8 (H_1, broad multiplet), 3.05 (H_4, broad multiplet obscured by OCH_3 signal), 3.05, 3.11 (O–CH_3, 3 H each, singlet), 4.6, 5.0 (CH_2–methylene broad multiplets), 5.98 (H_2, H_3, multiplet);[32] IR (neat) 1660 cm^{-1} (C=C). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.37; H, 8.60.

Table VI. Extinction Coefficient (ε) of 5-Methylene-1,3-cyclohexadiene (MCH) at Various Wavelengths (λ)

λ, nm	ε[a]	solvent
303[b]	4400[c]	isooctane
303	4580[d]	decane
343	1000[e]	benzene
350	520[e]	benzene
360	150[e]	benzene
370	31[e]	benzene

[a] Determined by dilution of weighed amounts of MCH unless otherwise noted. [b] Wavelength of maximum absorption. [c] Reference 3. [d] Determined by colorimetric titration with diphenylpicrylhydrazyl (DPPH, $\epsilon_{508} = 1.08 \times 10^4$). [e] Dr. M. Iino, this laboratory.

5-Methylenebicyclo[2.2.1]2-en-7-one (5). To 3 mL of 3 M sulfuric acid in a round-bottom flask was added 1.36 g (8.2 mmol) of **4**. The mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with 10 mL of water and then extracted with three 25-mL portions of methylene chloride. The organic layer was washed with equal volumes of water, bicarbonate, and water again. The extract was then dried over anhydrous sodium sulfate and the solvent removed under vacuum. The residue was bulb-to-bulb distilled (0.05 torr) from a room temperature flask into a flask cooled with a dry ice–acetone slurry. A good yield (0.59 g, 60%) of ketone was obtained: ^1H NMR (CCl_4) δ 1.98 (H_n, dt, $J_{n,e}$ = 16 Hz, $J_{n;8,9} \simeq 2.5$ Hz), 2.66 (H_e, multiplet, $J_{e,n} \simeq 16$ Hz, $J_{e,1} \simeq 4$ Hz, $J_{e,8}$ and $J_{e,9} \simeq 2.5$ Hz), 2.98 (H_1, broad multiplet), 3.28 (H_4, broad multiplet), 4.83, 5.08 (H_8, H_9, CH_2–methylene, triplets, J = 2.5 Hz), 6.55 (H_2, H_3, multiplet);[33] IR (neat) 1790 (C=O), 1660 (C=C) cm^{-1}; UV (EtOH) 280 nm ($n \rightarrow \pi^*$); 2,4-DNP, mp 78–81 °C.

5-Methylene-1,3-cyclohexadiene (MCH). The ketone **5** (80 mg) was vacuum-transferred through a Pyrex tube (8 mm × 5 cm) heated to 230 °C at 0.6 torr. The effluent was condensed in a trap cooled with liquid nitrogen. Pure MCH was isolated by preparative GLC, giving a 13% yield. Toluene was formed also. The MCH/toluene ratio was 93:7. MCH was identified by GLC retention time by comparison with an independently prepared sample[34] and by the UV and ^1H NMR spectra: ^1H NMR (benzene-d_6) δ 3.1 (2 H, broad m), 4.8 (2 H, broad m), 5.7 (2 H, broad m), 6.1 (2 H, broad m); UV λ_{max} 303 nm. Table VI lists extinction coefficients at various wavelengths. The mass spectra of MCH and toluene are essentially identical when run on a Perkin-Elmer RMS-4 spectrometer with electron impact ionization. Rearrangement of the molecular ions to the tropylium cation must occur rapidly for both compounds.[35]

Sample Preparation. Due to the air sensitivity of MCH, samples were prepared in degassed solvents. The appropriate quantity of solvent was vacuum-transferred or pipetted into a two-neck glass vessel equipped with a greaseless high vacuum stopcock and a serum cap. The solvent was degassed by repeated freeze–thaw cycles while attached to a vacuum at 5×10^{-4} torr. The vessel was pressurized with Ar, and a 20-cm stainless steel needle bent at a right angle conducted the He effluent containing MCH from the GLC through the serum cap and into the solvent, kept cold by immersing the vessel in a slush bath. The stopcock was closed between collections to maintain an inert atmosphere.

When sufficient MCH had been collected, the solution was again degassed by freeze–thawing and then vacuum-transferred to a 10-mL drying ampule, a UV cell, or an NMR tube and sealed. The receiving vessels had been cleaned and conditioned by washing with NaOH solution, then rinsing thoroughly with distilled water, and finally drying at 110 °C for several hours.

The disappearance of MCH in solution was followed by continuously monitoring the UV absorbance of a sample held in the thermostated compartment of a Gilford-modified Beckman DU or by immersion of an ampule of the sample in an oil bath and removing samples at frequent intervals. The wavelength used was determined by the initial concentration of MCH and the spectrum of the solvent. Extinction coefficients were determined at several wavelengths and are summarized in Table VI. The spectra were monitored, in general, through at least two half-lives.

Styrene polymerization rates were determined gravimetrically by precipitation of the polymer in cold methanol. The styrene solution (ca. 5 mL) was first diluted with a small amount of toluene (2–3 mL) and then very slowly pipetted with stirring into 400 mL of reagent grade methanol at 10 °C. The precipitated polymer was filtered on a medium porosity sintered glass funnel and brought to constant weight under vacuum at room temperature.

The chain transfer constant of MCH was determined by standard methods[36] from the intrinsic viscosity of polymer solutions in benzene at 30 °C. Solutions of MCH in styrene were initiated by 1.8×10^{-2} M AIBN (freshly recrystallized from EtOH). As a check on the method, we found $C = 8.1$ for butanethiol (literature values are 5.4–22.0[27]).

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Registry No.—AH, 23808-23-3; MCH, 20679-59-8; **2**, 2207-27-4; **3**, 37418-57-8; **4**, 68582-38-7; **5**, 65283-95-6; styrene, 100-42-5; hexachlorocyclopentadiene, 77-47-4; allene, 463-49-0.

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(10) This analysis also assumes that no AH is carried over upon distillation or vacuum-transfer of styrene during the purification and prepolymerization steps and that the concentration of AH is in fact (nearly) zero at time zero. No control experiments have ever been reported to probe whether or not this assumption is reasonable.

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(18) A referee has pointed out the possibility that 5-methylene-1,3-cyclohexadiene (MCH) may act not only as an initiator but at the same time as an inhibitor, exactly balancing out its ability to initiate the polymerization of styrene. It has been reported that certain polyenes do indeed inhibit the thermal polymerization of styrene.[19] Such copolymerizations were studied using rather high concentrations (ca. 1 M) of added polyene; for example, about 1 M 3,5,7-decatriene lowers the rate of polymerization by a factor of only 25.[19c] Our studies with MCH were done at concentrations of only 0.01 M or less, and unless CH is a much better inhibitor than decatriene a very much smaller effect is expected. Our data show that the rate of polymerization of styrene is unchanged, within experimental error, over a 40-fold range in initial MCH concentration. Furthermore, if MCH is an inhibitor, then the styrene Diels–Alder dimer (AH) must also be. It seems very unlikely that the initiating and inhibiting abilities are exactly balanced out in the case of both MCH and compound **12** but not in the case of AH.

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(21) (a) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **6**, 16 (1967). (b) There are two isomers, with the phenyl substituent either axial or equatorial, that have different steric requirements in the MAH reaction with styrene. Models indicate that both isomers react with styrene in transition states that are more congested than is that for MCH–styrene. Recently, H. F. Kauffman, O. F. Olaj, and J. W. Breitenbach [*Makromol. Chem.*, **177**, 939 (1976)] have discussed this and conclude that only the isomer with an axial phenyl substituent initiates styrene.

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(26) There is some question as to the size of the chain transfer constant of styrene monomer. As has been pointed out,[16] the experimentally observed value assuming all transfer occurs to monomer is too large. We have used a value of 1×10^{-5} for C_M, slightly larger than the chain transfer constant of benzene but smaller than the transfer constant of ethylbenzene.[27] This value is consistent with that which can be calculated (eq 10) from the degree of polymerization at low conversions.[16,25] We have then calculated from eq 10 the chain transfer constant of AH to fit the observed $\bar{P}_n$ at high conversions. The value obtained, $C_{AH} = 8$, seems reasonable when compared to the experimentally determined chain transfer constant of MCH.

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(30) W. R. Dolbier and S.-H. Dai, *J. Am. Chem. Soc.*, **94**, 3948 (1972).

(31) See J. C. Davis and T. V. van Auken, *J. Am. Chem. Soc.*, **87**, 3900 (1965), E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964), and P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1171 (1964), and **85**, 2709 (1963), for studies of norbornene ^{1}H NMR.

(32) At 100 MHz this multiplet has five lines showing other slight splittings. At 60 MHz the multiplet collapses to three lines.

(33) At both 60 and 100 MHz this multiplet has three lines.

(34) The sample was prepared by the method of Bailey.[3]

(35) Cf. R. M. Silverstein and G. C. Basser, "Spectrometric Identification of Organic Compounds", 2nd ed., Wiley, New York, N.Y., 1967, p 16.

(36) E. A. Collins, J. Bares, and F. W. Billmeyer, Jr., "Experiments in Polymer Science", Wiley, New York, N.Y., 1973, p 398; G. Odian, "Principles of Polymerization", McGraw-Hill, New York, N.Y., 1970, p 205–212; F. R. Mayo, R. A. Gregg, and M. S. Matheson, *J. Am. Chem. Soc.*, **73**, 1691 (1961).