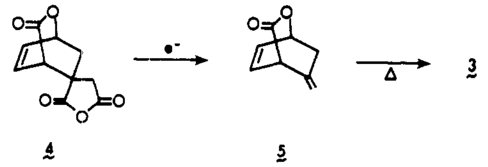
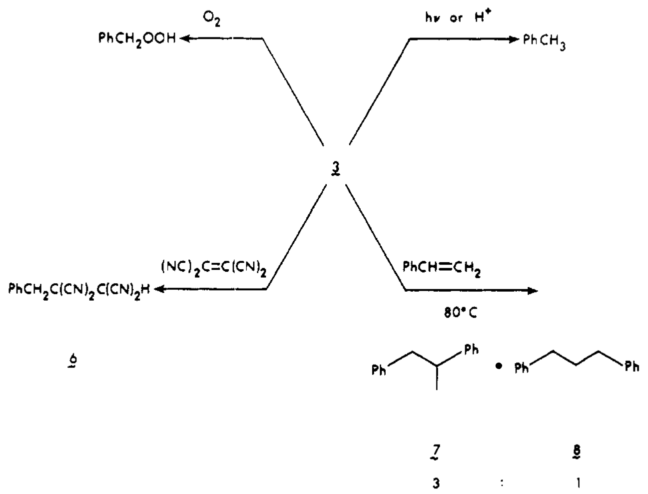
Scheme II



Scheme III



form the adduct 4,[6,7] mp 144–146 °C, 27%. Electrolysis[9] of 4 produced 5,[6] mp 11–14 °C, 45%.

The rate of thermolysis of 5 is great enough, at 60 °C $k_1 \sim 2.5 \times 10^{-7}$ s^{-1},[10] so that thermolysis of a ~10^{-1} M solution of 5 in styrene should result in formation of radicals at a rate greater than the thermal rate of formation of radicals in styrene, at 60 °C $k_i = 1.3 \times 10^{-10}$ mol L^{-1} s^{-1},[11] if hydrogen atom transfer from 3 to styrene were efficient. However, after heating styrene containing 0.1 M 5 at 80 °C for 2 h only 80% as much of a less crystalline polymer was isolated by precipitation with ethanol as was isolated from control runs. Evaporation of styrene under vacuum left <5% more residue, after correction for remaining 5, than was left in control runs. Thus, 5 appears to act only as a chain transfer agent and not as an initiator.

Injection of ether solutions of 5 into a gas chromatograph (GC) produced 65% 3, 5% toluene, and a trace of benzene.[12] Pure (GC) 3[13] was trapped from the effluent of the GC. Reactions of 3 that were studied are shown in Scheme III. It is quite stable in the absence of oxygen or acid.

In degassed cyclohexane a 10^{-4} M solution of 3 is indefinitely stable at 20 °C and at 60 °C 3 is slowly isomerized to toluene, $t_{1/2} \sim 130$ h. Rapid isomerization, $t_{1/2} = 23$ min, of 3 to toluene occurred in a cyclohexane solution containing 10^{-4} M 3 and 5×10^{-4} M Cl_3CCO_2H at 20 °C. Atmospheric oxygen slowly oxidizes 3 to benzyl hydroperoxide.[14] Photolysis ($\lambda >$ 2800 nm) of 3 in cyclohexane produced toluene as the major product. Treatment of 3 with tetracyanoethylene (TCNE) resulted in a rapid reaction to form the ene adduct 6[6,15] as the only detectable adduct. Thermolysis of 5 in the presence of TCNE also formed 6.

At 80 °C there is a rapid reaction, $t_{1/2} \sim 6$ min, between 3 and styrene to form 7 and 8 in a 3:1 ratio in 90% total yield. About 5–8% toluene is formed also. No extra polymer is formed in styrene containing 2×10^{-3} M 3 after 12 min at 80 °C when 60–70% of 3 is consumed. Hydrogen atom transfer from 3 to styrene followed by coupling of the resulting benzyl and 1-phenylethyl radicals could be the route by which 7 is formed, but such a simple radical route to 8 is not available. Also, the lack of formation of extra polymer indicates that if radicals are formed they must all be consumed by coupling and disproportionation before addition to styrene can occur. It is unlikely that this would happen. Both 7 and 8 can be formed by a concerted ene reaction.[16] Reaction of unsymmetrical enophiles with alkenes has been shown to produce mixtures of products.[17]

The experiments reported here provide no evidence that 3 can function as an initiator of styrene polymerization. In this respect the behavior of 3 is quite different from that attributed to 1 and found for the synthetic analogue 2.[4] Isolation of a trimer corresponding to the coupling product of the radicals shown in Scheme I[18] indicates that 1 and 3 may have one reaction with styrene in common.

A careful kinetic study also has shown that 3, prepared by an independent route, does not initiate the polymerization of styrene.[19]

References and Notes

(1) (a) Presented at the 59th Canadian Chemical Conference of the Chemical Institute of Canada, London, Ontario, June 1976, Abstract OR-72. (b) This research was supported by a grant from the National Research Council of Canada.

(2) (a) F. R. Mayo, *J. Am. Chem. Soc.*, **75**, 6133–6141 (1953); (b) **90**, 1289–1295 (1968).
(3) For a critical, comprehensive review, see W. A. Pryor and L. D. Lasswell, *Adv. Free Radical Chem.*, **5**, 27–100 (1975).
(4) W. A. Pryor, J. H. Coco, W. H. Daly, and K. N. Houk, *J. Am. Chem. Soc.*, **96**, 5591–5593 (1974).
(5) W. J. Bailey and R. A. Baylouney, *J. Org. Chem.*, **27**, 3476–3478 (1962).

(6) Satisfactory spectral data and elemental analyses within ±0.3% of theory were obtained.

(7) The structure given is tentative. It has not been determined whether the anhydride group is endo or exo. The spiro ring junction was located by analogy with other Diels–Alder reactions of reactants containing carbonyl groups.[8]

(8) K. Alder, M. Schumacher, and O. Wolff, *Justus Liebigs Ann. Chem.*, **564**, 79–96 (1949).
(9) M. H. Westberg and H. J. Dauben, Jr., *Tetrahedron Lett.*, 5123–5126 (1968).

(10) Extrapolated from rates obtained at higher temperatures: k_1 = 9.26, 21.2, and 197 × 10^{-6} s^{-1} at 100, 110, and 140 °C, respectively, in C_6D_6 or CCl_4. Rates were determined by monitoring solutions of 5 by ^1H NMR. First-order kinetics were obtained over at least 3 half-lives.

(11) K. E. Russell and A. V. Tobolsky, *J. Am. Chem. Soc.*, **75**, 5052–5054 (1953).

(12) Injection port 400 °C, Carbowax 1000 column, 70 °C. Benzene was identified by its retention time and by its mass spectral cracking pattern. Its mode of formation is unknown.

(13) NMR (C_6D_6) τ 3.87–4.68 (4 H, complex multiplet), 5.25 (2 H, complex multiplet), 6.93 (2 H, complex multiplet); UV λ_{max} (C_6H_{12}) 303 nm (ϵ 4400); IR ν_{max} (CCl_4) 3075 (m), 3035 (s), 1595 (s), 1400 (s), 863 (s), 647 (s) cm^{-1}. The UV data is the same as that previously reported,[5] but the IR data is somewhat different. The mass spectral cracking pattern obtained on electron impact is identical with those of toluene and of cycloheptatriene, but that obtained by chemical ionization (CH_5^+) is different from that of toluene.

(14) The ^1H NMR signals due to 3 of a ~0.1 M solution in C_6D_6 containing a drop of D_2O kept under air disappeared over a period of several days and were replaced by signals at τ 2.85 (5 H, m) and 5.31 (2 H, s).

(15) NMR (CD_3COCD_3) τ 2.46 (5 H, s), 4.0 (1 H, s), 6.21 (2 H, s). Material of the same melting point previously isolated was formulated as the Diels–Alder adduct.[5]

(16) For a review of the ene reaction see H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 556–557 (1969).
(17) K. Alder and H. von Brachel, *Justus Liebigs Ann. Chem.*, **651**, 141–153 (1962).
(18) J. Kurze, D. J. Stein, P. Simak, and R. Kaiser, *Angew. Makromol. Chem.*, **12**, 25–41 (1970).

(19) W. A. Pryor, W. D. Graham, and J. G. Green, *J. Org. Chem.*, following communication in this issue. We thank Professor Pryor for informing us of these results before publication.

Karl R. Kopecky,* Ming-Pui Lau
Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada T6G 2E1

Received August 22, 1977

Radical Production from the Interaction of Closed-Shell Molecules. 5. The Chemistry of Methylenecyclohexadiene[1]

Summary: 5-Methylene-1,3-cyclohexadiene (MCH) has been studied as a model for the Diels–Alder dimer of styrene (AH), which is postulated to be involved in radical production in the

0022-3263/78/1943-0526$01.00/0

Table I. A Comparison of Data for AH and MCH in 8.35 M Styrene at 60 °C

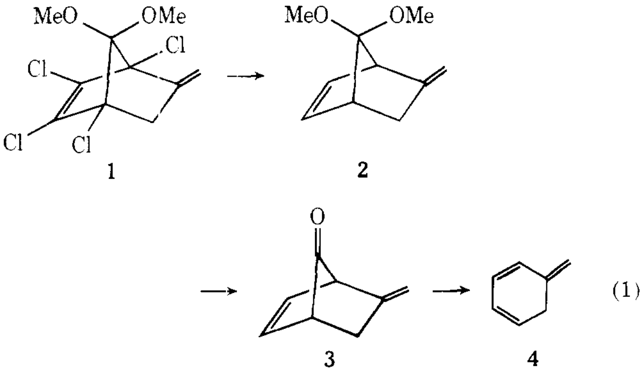
Compd	k_{dis}, $M^{-1} s^{-1}$[a]	$R_P \times 10^6$[b]	$\bar{P}_n \times 10^{-4}$[c]	C[d]	% MAH[e]
AH	0.9×10^{-5}[f]	2.0[g]	1.0[g]	1[h]	1
MCH	5.3×10^{-5}[i]	2.0[j]	0.2[k]	9[l]	<0.01

[a] Pseudo-unimolecular rate constant for disappearance of the compound in styrene, determined using UV absorption. [b] Rate of polymerization of styrene, M s^{-1}. [c] Number-average degree of polymerization. [d] Transfer constant; i.e., the ratio of rate constants for chain transfer and propagation, ref 2b. [e] Percent of the compound that disappears in reactions that produce radicals (other than by transfer) capable of initiating styrene's polymerization. [f] Calculated from the rate of formation of AH assuming a steady-state concentration of 6.5×10^{-5} M, ref 16. [g] For thermal polymerization, ref 15 and 17. [h] Reference 22. [i] From disappearance of MCH followed at 360 nm. [j] Determined by precipitation at 0.0004–0.012 M MCH. [k] At 1×10^{-4} M MCH. [l] Approximate value, see text.

spontaneous polymerization of styrene. Attempts to rationalize the different rates of radical production from MCH and AH are presented.

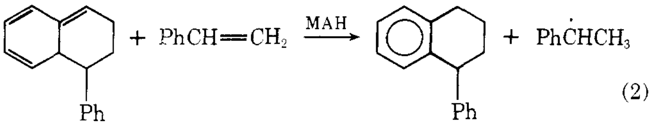
Sir: The acceleration of the homolytic scission of bonds in one molecule by interaction with another molecule is of considerable theoretical[1,2] and practical[3] significance. Of these reactions, the molecule-assisted homolysis (MAH) of a C–H bond in the presence of olefins is the most intriguing to organic chemists, and several such processes have now been identified.[1–4] With the aim of studying a particularly simple example of such a process, we have examined the reactions of 5-methylene-1,3-cyclohexadiene (MCH) with styrene.

The synthesis of MCH (4) has been reported by Bailey and Baylouny,[5] but isolation of MCH from the dilute pentane solution obtained in their method requires repetitive GLC. We sought a route involving a less tedious isolation and purification procedure; our synthesis is outlined in eq 1. Compound 1[6,7] when treated with sodium and *tert*-butyl alcohol in tetrahydrofuran gives a 31% yield of 2.[8] The ketal 2 can be hydrolyzed to 3 with 3 M H_2SO_4 at room temperature in 60% yield.[9] Ketone 3 decarbonylates under a variety of conditions to give MCH.[10] The most convenient method consists of a bulb-to-bulb transfer of neat ketone at 0.5 mmHg through a tube heated to 250 °C. The product was isolated by GLC.[11]



1 2 3 4 (1)

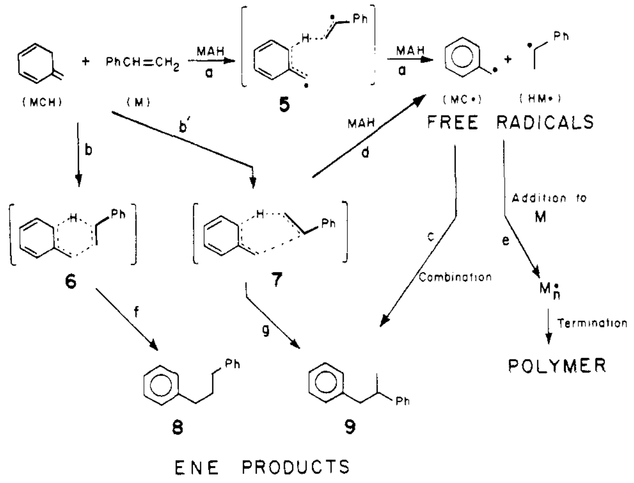
There is a considerable body of evidence that has been interpreted as demonstrating that the mechanism of initiation of the thermal polymerization of styrene is the MAH reaction of the styrene Diels–Alder dimer, AH, with another styrene molecule, eq 2.[3,12] It appeared likely that MCH would also



AH M A· HM (2)

undergo an MAH reaction with styrene and initiate polymerization, as shown in Scheme I.

Scheme I



Surprisingly, however, MCH does not initiate the polymerization of styrene. Concentrations of MCH from 0.004 to 0.012 M produce rates of polymerization equal to the thermal rate, within experimental error. Furthermore, methyl acrylate, which does not undergo spontaneous polymerization, is not initiated by concentrations of MCH as high as 0.01 M. However, MCH does disappear rapidly in both styrene and methyl acrylate (as monitored by UV).

Scheme I outlines possible reactions of MCH (or AH). Kopecky and Lau,[13] who independently have found that MCH does not initiate the polymerization of styrene, have reported that MCH undergoes an ene reaction[14] with styrene to give both 8 and 9. Product 8 can best be rationalized by reactions b and f of Scheme I. Product 9 could arise from analogous processes, eq b′ and g; however, since the parallel reactions of AH and related species[4] lead to scavengable free radicals, product 9 might result from reactions a and c, or b′-d-c as well.

Table I shows a comparison of data for AH and MCH in styrene at 60 °C. Based on the known rate of polymerization of styrene[15] and our measured rate of the pseudo-unimolecular disappearance of AH in styrene, k_{dis}[AH],[16] only a small

$$R_i = \frac{2k_t R_p^2}{k_p^2 [M]^2} = 2k_{dis} f [AH] \qquad (3)$$

fraction, $f \simeq 0.011$, of the AH reacts in styrene to give scavengable radicals (cf. eq 3[17]). Most of the AH gives ene products via reactions b, b′, or c in Scheme I. A small amount of AH is consumed by chain transfer.

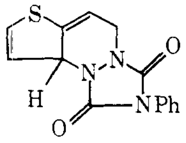
The rate constant for disappearance of MCH in styrene is six times larger than that of AH (Table I). However, a more rapid ene reaction alone cannot account for the lack of detectable free-radical production from MCH. If it is *assumed* that MCH undergoes an assisted homolysis with the same rate constant as does AH, then 10^{-2} M MCH is sufficiently concentrated so that an increased rate of polymerization should be observed. This is true even if a rapid ene reaction (and/or chain transfer) of MCH consumes 99.9% of the MCH and only

0.1% undergoes an MAH reaction. In order to explain the observed lack of initiation, MCH must have a rate constant for MAH reaction that is at least 20 times smaller than that of AH.[18]

Two types of transition states for the MAH reaction of MCH (or AH) could be envisioned: (1) a cyclic, ene-like transition state (**7**) could give scavengable radicals via eq d;[19] or (2) the MAH transition state might involve an open, extended conformation (**5**) in which the radical centers are formed far apart. Radicals formed in this process may combine to form ene-type products (eq c) or diffuse apart (eq e) and initiate polymerization.

This formulation of ene and MAH processes suggests a possible rationale for the larger yield of radicals from AH–styrene than from MCH–styrene. The ene reaction is known to be sensitive to steric effects,[20] and models indicate that the repulsive interactions in transition states like **6** or **7** would be greater for AH than for MCH. This may force a larger fraction of the AH–styrene interactions to adopt the extended transition state **5**, or to have more radical character in transition state **7**, giving a greater yield of radicals via reaction d. In addition, it should be noted that the potential 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.

As might be expected, MCH is an excellent transfer agent. The transfer constant of MCH is approximately 9 at 60 °C.[21] This is by far the largest transfer constant ever reported for a hydrocarbon. Since the value is so large, it is difficult to measure precisely;[21b] however, there is no doubt that MCH is an excellent transfer agent, as good or better than AH ($C = 1$)[22] or BH ($C = 5$), another model of AH that we reported on previously.[4]



BH

Finally, some comments should be made about the implications of the present work on the mechanism of the thermal polymerization of styrene.[1b] Our *a priori* expectation was that MCH would initiate polymerizations. The fact that it does not can be rationalized in one of two ways. (1) It can be assumed that MCH is a poor model for AH, because ene reactions involve variable transition states with differing amounts of radical character, or because AH donates a tertiary hydrogen and yields a tertiary radical whereas MCH donates a secondary hydrogen to yield a primary radical, or for some other reason. (2) Or the MAH mechanism for the *initiation* of polymerization of styrene by AH can be rejected. A critical review[1b,3] of the evidence supporting the AH mechanism indicates overwhelming support for the *presence* of AH in thermal polymerizations of styrene and *transfer* by AH, but an absence of *unambiguous* evidence that AH undergoes an assisted homolysis step (eq 2). However, if the AH mechanism for styrene is rejected, it is difficult to suggest an alternative.[1b] (One alternative possibility is the diradical transfer mechanism that we have recently suggested for pentafluorostyrene.[23])

It seems most reasonable and economical at present to continue to accept the Diels–Alder mechanism for styrene, but with the realization that the critical MAH step, eq 2, has *not* been explicitly established. Clearly, the critical experiment is the synthesis and testing of AH itself, and we are now attempting this.[1b]

Acknowledgment. We wish to thank the National Science Foundation for partial support of this work and Dow Chemical Company for a grant to William A. Pryor. We also wish to express our appreciation to Dr. Masashi Iino for preliminary studies, Mary G. Sorci for polymer solution viscosity measurements, and Dr. Eric G. Olsen for helpful suggestions.

References and Notes

(1) (a) These results have been presented: W. A. Pryor, *Abstracts, 174th National Meeting of the American Chemical Society*, Chicago, Ill., Sept. 1977, No. ORGN 88; (b) W. A. Pryor in "Organic Free Radicals", W. A. Pryor, Ed., American Chemical Society, Washington, D.C., in press.

(2) (a) N. N. Semenov, "Some Problems of Chemical Kinetics and Reactivity", Vol. I, translated by J. E. S. Bradley, Pergamon Press, New York, N.Y., 1958, pp 260–271; (b) W. A. Pryor, "Free Radicals", McGraw-Hill, New York, N.Y., pp 119–126, 184–186, 290.

(3) For a review see: W. A. Pryor and L. D. Lasswell in "Advances in Free Radical Chemistry", Vol. V, G. H. Williams, Ed., Academic Press, New York, N.Y., 1975, pp 27–99.

(4) W. A. Pryor, J. H. Coco, W. H. Daly, and K. N. Houk, *J. Am. Chem. Soc.*, **96**, 55591 (1974).

(5) W. J. Bailey and R. A. Baylouny, *J. Org. Chem.*, **27**, 3476 (1962).

(6) P. G. Gassman and J. L. Marshall, *Org. Synth.*, **48**, 68 (1968).

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

(8) NMR (CCl_4) δ 6.02 (t, 2-H), 4.88 (m, 1-H), 4.64 (m, 1-H), 3.12 (s, 3-H), 3.05 (s, 3-H), 2.8 (brm, 1-H), 2.6 and 2.3 (m, 1-H), 1.76 and 1.53 (t, 1-H).

(9) NMR (CCl_4) δ 6.56 (t, 2-H), 5.08 (t, 1-H), 4.83 (t, 1-H), 3.3 (m, 1-H), 3.0 (m, 1-H), 2.9 and 2.6 (m, 1-H), 2.15 and 1.88 (t, 1-H). 2,4-DNP: mp 78–81 °C.

(10) Identified by GC retention time, UV, and NMR. The decomposition of the ketone was first order in CCl_4 solution with a half-life of 4440 s at 93 ± 1 °C and 380 s at 112 ± 1 °C. MCH is both air and acid sensitive and must be handled accordingly.

(11) A 10% OV-1 on Chromosorb W 60/80 (5 ft × $\frac{1}{4}$ in.) column was used at 30–40 °C and 20 mL/min He flow.

(12) F. R. Mayo, *J. Am. Chem. Soc.*, **75**, 6133 (1953); **90**, 1289 (1968).

(13) K. R. Kopecky and M. P. Lau, *J. Org. Chem.*, preceding communication in this issue. We thank Professor Kopecky for allowing us to see a preprint copy of this manuscript.

(14) For a review of the ene reaction see H. M. R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969).

(15) R. H. Boundy and R. F. Boyer, "Styrene: Its Polymers, Copolymers, and Derivatives", Reinhold, New York, N.Y., 1952, p 216.

(16) Both K. Buchholz and K. Kirchner [*Makromol. Chem.*, **177**, 935 (1976)] and W. A. Pryor and R. A. Patsiga [*Spectrosc. Lett.*, **2**, 61 (1969) and unpublished data] have followed the rate of appearance of AH using an ab*sorption band* at 310–320 *nm* assumed due to AH. Since the rates of appearance and disappearance of AH can be assumed to be equal at the steady state, these data can be used to calculate the total rate of AH disappearance. The data at 64 °C of Buchholz and Kirchner were used here to obtain the pseudo-unimolecular total rate of disappearance of AH, $k_{dis}[AH]$.

(17) M. S. Matheson, E. E. Auer, E. B. Bevilaqua, and E. J. Hart, *J. Am. Chem. Soc.*, **73**, 1700 (1951); W. A. Pryor, "Free Radicals", McGraw-Hill, New York, N.Y., 1966, p 237.

(18) This calculation assumes no ene product results from free-radical processes; i.e., eq c, Scheme I, is not significant.

(19) *Indeed some ene reactions* appear to involve radicals, since they are sensitive to free-radical initiators and inhibitors; cf. W. A. Thaler and B. Franzus, *J. Org. Chem.*, **29**, 2226 (1964); R. Huisgen and H. Pohl, *Chem. Ber.*, **93**, 527 (1960).

(20) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **6**, 16 (1967).

(21) (a) From AIBN initiated polymerizations of styrene containing $\sim 10^{10-4}$ M MCH. For treatment of data cf. E. A. Collins, J. Bares, and F. W. Billmeyer, Jr., "Experiments in Polymer Science", Wiley, New York, N.Y., 1973, p 398; F. R. Mayo, R. A. Gregg, and M. S. Mathieson, *J. Am. Chem. Soc.*, **73**, 1691 (1951); G. Odian, "Principles of Polymerization", McGraw-Hill, New York, N.Y., 1970, pp 205–212. (b) By parallel methods, we obtain $C = 9$ *for butanethiol*.

(22) W. A. Pryor and J. H. Coco, *Macromolecules*, **3**, 500 (1970).

(23) W. A. Pryor, M. Iino, and G. R. Newkome, *J. Am. Chem. Soc.*, **99**, 6003 (1977).

William A. Pryor,* W. David Graham
John Glass Green

Louisiana State University, Department of Chemistry
Baton Rouge, Louisiana 70803

Received August 23, 1977