(24S)-6β-Methoxy-3α,5-cyclo-5α-ergostan-25-ol (17): ^{1}H NMR (400 MHz) δ ($CDCl_3$) 3.324 (s, 3 H, OMe), 1.165 (s, 3 H, C26 or 27), 1.153 (s, 3 H, C26 or 27), 1.021 (s, 3 H, C19), 0.932 (d, J = 6.5 Hz, C21), 0.892 (d, J = 6.8 Hz, 3 H, C24), 0.714 (s, 3 H, C18); low-resolution mass spectrum, m/z (relative intensity) 430 (M^+, $C_{29}H_{50}O_2$, 8), 415 (7), 398 (9), 375 (14), 255 (14), 213 (12), 105 (59), 59 (100), 55 (67).

Dehydration of (24S)-6β-Methoxy-3α,5-cyclo-5α-ergostan-25-ol (17). Treatment of **17** as described above gave a 1:1 mixture of codisterol (**18**) and 24-methyldesmosterol (**19**) as their *i*-methyl ethers.

Hydroboration of Stigmasterol *i*-Methyl Ether (6A-M). A solution of 392 mg of **6A-M** in 5 mL of THF was treated with 15 mL of 1 M BH_3/THF. After 4.5 h at room temperature and 1 h at 67 °C, the reaction mixture was worked up as described above. Separation by HPLC gave **7A-M** (21%), an unidentified epimeric steroidal side chain alcohol (8%), **4A-M** (6%), **9A-M** (32%), a 1:1 mixture of (24*R*,28*S*)-6β-methoxy-3α,5-cyclo-5α-stigmastan-28-ol (**16a**) and its 24*R*,28*R* epimer (**16c**)[13] (29%), and **5A-M** (4%).

Isomerization of Fucosterol *i*-Methyl Ether (14-M). a Solution of 67.9 mg of **14-M**[20] in 5 mL of THF was treated with 5 mL of 1 M BH_3/THF at 0 °C under Ar. After 6 h 4.5 mL of 5% NaOH and 3 mL of H_2O_2 were added. After 12 h at 0 °C the mixture was worked up as described above to give 52.1 mg of a mixture of (24*R*,28*S*)-6β-methoxy-3α,5-cyclo-5α-stigmastan-28-ol (**16a**) and its 24*S*,28*R* epimer (**16b**).[13] Treatment of 43.3 mg of this mixture with phosphorus oxychloride as described above gave, after chromatography, 37.8 mg of isofucosterol *i*-methyl ether (**15-M**) (91%) containing 16% **14-M**.

Dehydration of (24R,28S)-6β-Methoxy-3α,5-cyclo-5α-stigmastan-28-ol (16a). Treatment of **16a** as described above gave pure **15-M**.

28-Deuterio-6β-methoxy-3α,5-cyclo-5α-stigmasta-24(28)-(Z)-diene (28-*d* 15-M).[18] A solution of (24*R*)-6β-methoxy-3α,5-cyclo-5α-stigmastan-28-one (**20**)[13] in ether was reduced with 5 mg of $LiAlD_4$. After 5 min the reaction was quenched with water and extracted with ether. Separation of the products by preparative TLC (benzene/ether, 9:1) followed by dehydration of the (24*R*,28*S*)-28-deuterio-6β-methoxy-3α,5-cyclo-5α-stigmastan-28-ol (**28-*d* 16a**) gave **28-*d* 15-M**.

Acknowledgment. Financial support was provided by NIH Grants No. GM-06840 and GM-28352. Use of the 400-MHz NMR spectrometer was made possible by NSF Grant No. CHE 81-09064. We wish to express our appreciation to Annemarie Wegmann-Szente for mass spectra. We thank the Swiss National Science Foundation for a grant to C.M. and the Upjohn Co. for a generous gift of stigmasterol.

(20) Pure fucosterol *i*-methyl ether was prepared by a copper allyl reaction: Giner, J.-L.; Margot, C.; Djerassi, C. *J. Org. Chem.*, submitted for publication.

Bimolecular Reactions of 3-Methylene-1,4-cyclohexadiene (*p*-Isotoluene), 5-Methylene-1,3-cyclohexadiene (*o*-Isotoluene), 1-Methylene-1,4-dihydronaphthalene (Benzo-*p*-isotoluene), and 9-Methylene-9,10-dihydroanthracene (Dibenzo-*p*-isotoluene)

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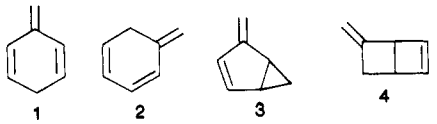
3-Methylene-1,4-cyclohexadiene, **1**, 5-methylene-1,3-cyclohexadiene, **2**, 1-methylene-1,4-dihydronaphthalene, **5**, and 9-methylene-9,10-dihydroanthracene, **8**, react with second-order kinetics in benzene solution. The activation parameters for the reaction of **1**, **5**, and **8**, especially the frequency factor, suggest a nonconcerted reaction with little orientational demand in the transition state. The frequency factor for the reaction of **2** suggests a concerted pathway. The product distribution from each compound reinforces the kinetic observations. The products from the pyrolysis of **1** could be rationalized by a radical cage intermediate, which could combine or disproportionate. The reaction products from **5** indicate a radical chain oligomerization. The reaction of **8** gives an insoluble solid. *o*-Isotoluene (**2**) gives ene dimers.

The existence of alicyclic isomers of toluene, *p*-isotoluene, **1**, *o*-isotoluene, **2**, *m*-isotoluene, **3**, and 5-methylenebicyclo[2.2.0]hexene, seemed unlikely a half century ago,[1] but all four compounds have been synthesized. Not unreasonably, both **1** and **2** are approximately 23 kcal/mol less stable than toluene as judged by gas-phase acidities compared with toluene.[2] However, the sensitivity of these materials to air, acid, and base precluded or obscured earlier efforts to observe their thermal behavior.



1 2 3 4

p-Isotoluene, **1**, was prepared by Plieninger and was reported to convert to toluene smoothly at room temperature. However, the conditions (in the presence of air, acid, or base) under which the isomerization of *p*-isotoluene occurred were not recorded.[3] A possible first-order, thermally allowed 1,5-hydrogen shift pathway for the isomerization of **1** was suggested by Dreiding.[4]

o-Isotoluene was synthesized by different routes by Bailey,[5a] Hasselmann,[5b] Kopecky,[5c] and Pryor.[5d] All previous experimenters reported that **2** forms toluene rapidly. The facile aromatization of *o*-isotoluene might be rationalized by the thermally allowed antarafacial 1,7-sigmatropic hydrogen shift.[4] Both Pryor and Kopecky proposed *o*-

(1) Horning, E. C. *Chem. Rev.* **1943**, *33*, 89.
(2) Bartmess, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 335.
(3) (a) Plieninger, H.; Maier-Borst, W. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 62. (b) Plieninger, H.; Maier-Borst, W. *Chem. Ber.* **1965**, *98*, 2504.
(4) Rey, M.; Huber, U. A.; Dreiding, A. S. *Tetrahedron Lett.* **1968**, 3583.
(5) (a) Bailey, W. J.; Baylouny, R. A. *J. Org. Chem.* **1962**, *27*, 3476. (b) Hasselmann, D.; Loosen, K. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 606. (c) Kopecky, K. R.; Lau, M.-P. *J. Org. Chem.* **1978**, *43*, 525. (d) Pryor, W. A.; Graham, W. D.; Green, J. G. *J. Org. Chem.* **1978**, *43*, 526.

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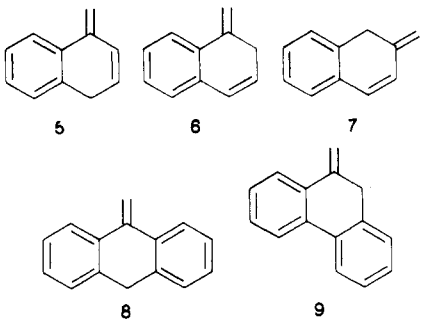
isotoluene as a model for the Diels–Alder dimer of styrene since the generally accepted mechanism for the self-initiated polymerization of styrene involves hydrogen atom transfer from the Diels–Alder dimer to styrene.[6a] However, *o*-isotoluene did not initiate the polymerization of styrene.[6b] Kopecky did find that **2** undergoes a formal ene reaction with styrene to yield $C_{15}H_{16}$ products.[5c] Pryor reported that a 10^{-3} M degassed benzene solution of *o*-isotoluene disappeared in a second-order process to form toluene.[5d]

Hasselmann observed that thermolysis of 5-methylenebicyclo[2.2.0]hex-2-ene, **4**, both in the gas phase (up to 200 °C) and in solution gave exclusively *o*-isotoluene, **2**. *o*-Isotoluene isomerized partially to toluene upon further reaction in the gas phase. In solution dimers were formed. Hasselmann suggested that *o*-isotoluene undergoes an ene reaction with **4** still present in solution to form $C_{14}H_{16}$ products.[5b]

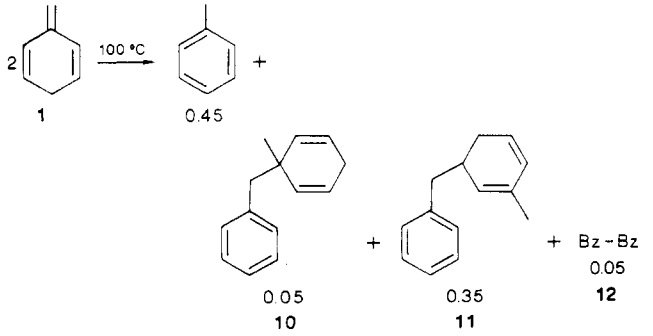
m-Isotoluene, **3**, has been reported to polymerize when pyrolyzed neat.[4]

Of the benzologues of *p*-isotoluene and *o*-isotoluene, namely, 1-methylene-1,4-dihydronaphthalene, **5**, 1-methylene-1,2-dihydronaphthalene, **6**, 2-methylene-1,2-dihydronaphthalene, **7**, 9-methylene-9,10-dihydroanthracene (dibenzo-*p*-isotoluene), **8**, and methylenedihydrophenanthracene, **9**, all but **5** have been reported.[7-10] The synthesis and reactions of **5** are reported here.

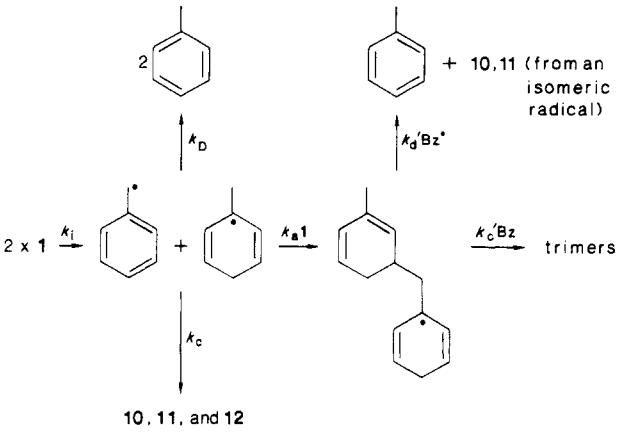


Results and Discussion

***p*-Isotoluene Pyrolysis.** A degassed benzene-d_6 solution of *p*-isotoluene, **1** (1 M), was pyrolyzed at 82, 100.5, and 122 °C and found to give toluene and C_{14} compounds: **10** is a ready 1:1 mol ratio (the ratio of the C_{14} products **10**, **11**, and **12** is 1:7:1).



Scheme I



Products **10** and **12** could be purified by GC separation on a SE-30 column. Subsequent NMR analysis indicated their identity [220-MHz NMR (**11**) δ 1.03 (s, 3 H), 2.4 (m, 2 H), 2.55 (s, 2 H), 5.43 (d, J = 10 Hz, 2 H), 5.57 (d, J = 10 Hz, 2 H), 7.2 (m, 5 H)]. Product **11** rearranged so it was identified after **10** and **12** were subtracted from the NMR spectrum of pyrolyzed *p*-isotoluene [220-MHz NMR (**11**) δ 1.68 (s, 3 H), 1.98 (AB q, 2 H), 2.2–2.7 (m, 2 H), 5.30 (br s, 1 H), 5.70 (br s, 2 H), 7.2 (m, 5 H)].

Second-order kinetics were observed up to 3 half-lives: $\log k_1$ (L/mols) = (8.1 ± 0.2) − (21 800 ± 300)/2.3RT. The energetics for the reaction of **1**, especially the frequency factor A ($10^{8.1\pm0.2}$), suggest a nonconcerted reaction with little orientational demand in the transition state. This observation should rule out formation of toluene by a 12-electron double hydrogen shift or the formation of dimer **11** by an ene reaction followed by a 3,3-shift. A process might be envisioned where toluene and the dimers (**10**, **11**, and **12**) can form from the disproportionation and combination products of the radicals resulting from rate-determining bimolecular hydrogen atom transfer from one *p*-isotoluene to another. After hydrogen atom transfer between two molecules of **1**, benzyl and 3-methylcyclohexadienyl can disproportionate (k_d) to form toluene or combine (k_c) to give C_{14} products (Scheme I).

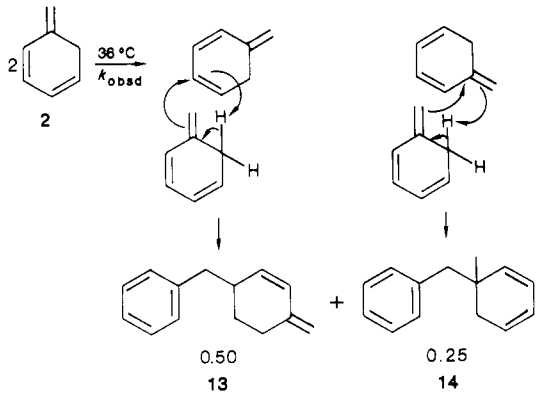
It would appear that the initially formed radical pairs react predominantly within a solvent cage since the presence of dimethylhydroxylamine (a good hydrogen donor) had no effect on the rate of reaction. Further, the reaction could not be initiated by AIBN nor was the rate of polymerization of styrene affected by reaction of *p*-isotoluene. The formation of 5% bibenzyl and small amounts of trimer probably occurs outside of the geminate pair via k_a **1** of Scheme I.

***p*-Isotoluene with AIBN.** A degassed benzene-d_6 solution of ca. 1×10^{-3} M **1** and 7.5×10^{-4} M AIBN was sealed in a reaction vessel (treated by washing with acetone, deionized water, and dilute ammonium hydroxide; followed by drying in an oven overnight). After pyrolysis for 4 h at 80 °C, **1** gave no more toluene or products **10**, **11**, and **12** than was obtained from the normal self-reaction under these conditions. All of the *p*-isotoluene was consumed, and 36% of the AIBN was converted to tetramethylsuccinonitrile. A GCMS of the product sample indicated that in addition to the formation of tetramethylsuccinonitrile, products derived from the addition of the dimethylcyanocarbinyl radical to *p*-isotoluene were formed (two GC fractions were eluted with molecular ions at m/e 159 and 161; both fractions contained the tropylium ion as the base peak and $(CH_3)_2C$ + CN ion).

The chain length was determined by the rate of reaction

(6) (a) Mayo, F. R. *J. Am. Chem. Soc.* **1953**, *75*, 6133. (b) Graham, W. D.; Green, J. G.; Pryor, W. A. *J. Org. Chem.* **1979**, *44*, 907.
(7) Scott, L. T.; Brunsvold, W. R. *J. Org. Chem.* **1979**, *44*, 641.
(8) Murata, I.; Nakazawa, T.; Kato, M.; Tatsuoka, T.; Sugihara, Y. *Tetrahedron Lett.* **1975**, 1647.
(9) Takagi, M.; Hirabe, T.; Nojima, M.; Kusabayashi, S. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1311.
(10) Sugimoto, A.; Yoneda, S. *J. Chem. Soc., Chem. Commun.* **1982**, 376.

Scheme II



of *p*-isotoluene (after the observed rate was corrected for by the normal reaction rate of *p*-isotoluene at 80 °C) and the rate of decomposition of AIBN.[11] On the assumption of an efficiency of 0.6 for AIBN,[12] the calculated chain length of the reaction of *p*-isotoluene with AIBN was ca. unity (0.98). Hence, the reaction of *p*-isotoluene with AIBN was not a radical chain mechanism but a bimolecular addition reaction.

Pyrolysis of *o*-Isotoluene. Second-order kinetics observed for the disappearance of *o*-isotoluene, **2**,[5d] is ca. 0.5 M benzene-d_6 solution at 10, 21, 36, and 58 °C; these gave $\log k_2$ (L/mol s) = (4.6 ± 1) − (11 800 ± 2000)/2.3RT. The frequency factor for **2** ($10^{4.6\pm1}$) suggests a concerted pathway, and the major products **13** and **14** from *o*-isotoluene are ene-type products (Scheme II).

The products had retention times similar to **10**–**12** and were separated by GC on a SE-30 column. Subsequent NMR analysis indicated their identity [220-MHz NMR of compound with exocyclic methylene group (**13**) δ 1.36 (sym m, 1 H), 1.77 (sym m, 1 H), 2.0–2.7 (m, 5 H), 4.69 (s, 1 H), 4.72 (s, 1 H), 5.42 (d, J = 10 Hz, 1 H), 6.07 (d, J = 10 Hz, 1 H), 7.2 (m, 5 H); 220-MHz NMR (**14**) δ 0.93 (s, 3 H), 2.07 (AB q, 2 H), 2.57 (AB q, 2 H), 5.46 (d, J = 10 Hz, 1 H), 5.8 (m, 3 H), 7.2 (m, 5 H)]. Toluene was not observed as a product in contrast to previous results.[5a-d] However, it was found that the *o*-isotoluene was exceedingly acid-sensitive, giving toluene; further, it could not be purified by preparative GC.

The relative facility for undergoing an ene reaction is a significant difference between the two isomers **1** and **2**. In the case of *o*-isotoluene, **2**, an aromatic system is generated directly via the ene pathway, but with *p*-isotoluene, **1**, only nonaromatic materials can be produced. Thus the exothermicity differences may be reflected in the relative transition state energies.

Benzo-*p*-isotoluene. Previously unknown benzo-*p*-isotoluene, **5**, was synthesized from 1-naphthoic acid by a route similar to that for preparation of *p*-isotoluene. The oxide of *N*,*N*-dimethyl-*N*-(1,4-dihydronaphthyl-1-methyl)amine eliminated smoothly to form benzo-*p*-isotoluene, **5**, at 85–105 °C under 0.5 mm. Further purification of **5** by preparative GC was not possible; all attempts yielded 1-methylnaphthalene. The benzo-*p*-isotoluene was used after the removal of dimethylhydroxylamine by acid–base treatment followed by solvent evaporation. Compound **5** was stored at −78 °C under nitrogen.

Benzo-*p*-isotoluene disappeared with second-order kinetics (at 82, 100.5, and 122 °C): $\log k_5$ (L/mol s) = (8.5 ± 0.7) − (22 300 ± 800)/2.3RT. The energetics for the reaction of **5**, especially the frequency factor A ($10^{8.5}$), suggest a nonconcerted reaction. The products from **5** indicate a radical chain oligomerization (Scheme III).

Analytical GC indicated that 1-methylnaphthalene was not a product since the ratio of 1-methylnaphthalene to an internal standard (naphthalene) remained constant throughout the pyrolysis. Analytical GC of a 1 M degassed sample of **5** in benzene pyrolyzed at 140 °C indicated the presence of three C_{22} products in the ratio 7:2:1. The existence of C_{22} compounds was verified by GCMS (three fractions were eluted with parent molecular peaks at m/e 282, 284, and 286). The combination products were separated, as a mixture, from oligomer by column chromatography over neutral alumina eluting with 1:19 chloroform–hexane. Proton NMR (360 MHz) of the mixture indicated the presence of 1,2-di(1-naphthyl)ethane **16** by the chemical shift of the methylene protons δ 3.5 (s, 4 H).[13] The presence of termination product **15** was deduced by the remaining NMR peaks: δ 2.0 (s, 6 H, 2 CH_3), 2.7 (m, 4 H, 2 CH_2 benzylic), 3.0 (d of m, 2 H, 2 CH allylic), 5.8 (d, 2 H, 2 CH vinylic), and aromatic protons. Comparison of the chemical shifts of compound **15** with previously known 4-methyl-1,2-dihydronaphthalene (**18**) supported the structural assignment of **15**. The NMR of **18** was determined by Wilt: δ 2.0 (CH_3), 2.25 (CH_2 allylic), 2.7 (CH_2 benzylic), 5.77 (CH vinylic), and aromatic protons.[14] The allylic protons in **15** are deshielded and therefore shifted downfield from the allylic protons in **18** (methine **15** versus methylene **18**).

The identity of the other possible termination product **17** was not established with certainty due to the small quantities present.

The structure and chain length (n − 1) of the oligomer were determined by proton NMR (90 MHz) after separation from combination products. The NMR indicated the presence of aromatic protons (δ 7.0–7.5), vinylic protons (δ 5.6–5.9), aliphatic protons (δ 2.3–3.2), and a minor methyl peak at (δ 2.0). The peaks are broad, which is characteristic of oligomers. The integrated proton ratios of the oligomer (Scheme III) gives the ratio four aromatic/one vinylic/five aliphatic protons.

The methyl group at δ 2.0 (which is structurally similar to the methyl group of compound **18** chemical shift δ 2.0) was assigned to oligomer termination or initiation. Statistics suggest a 1:2:1 ratio of two methyl groups/one methyl group/no methyl groups per oligomeric unit, depending on the mode of termination and initiation, or an average of one methyl group per oligomeric unit. Integration of the methyl group gives three units, and vinylic protons 12 units, hence the chain length could be calculated:

$$\frac{\text{12 units/H vinylic}}{\text{1 unit/H methyl}} = 12 = n$$

A possible mechanistic scheme for the self reaction of **5** can be a radical chain mechanism where the initiation step again involves hydrogen atom transfer between two molecules of benzo-*p*-isotoluene, **5**. The newly formed radicals can either terminate by combination, yielding combination products, or add to more **5**, forming longer radical units as in Scheme I. Oligomer termination in-

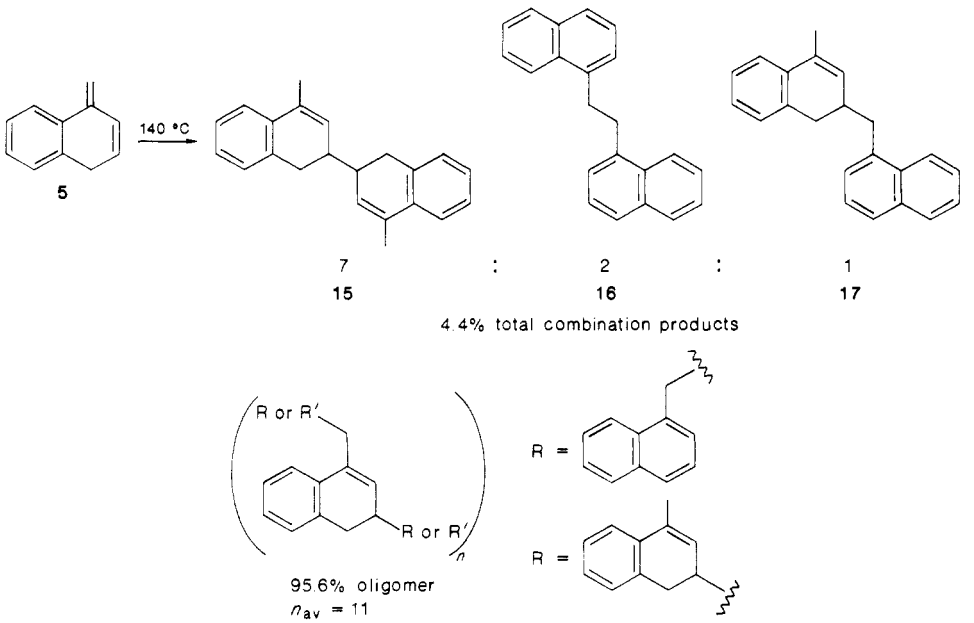
(11) Log k (/s) = 15–30 800/2.3RT for AIBN decomposition. Bamford, C. H.; Barb, W. G.; Jenkins, A. D.; Onyon, P. F. *The Kinetics of Vinyl Polymerization by Radical Mechanism*; Academic Press Inc.: New York, 1958; p 141.

(12) Pryor, W. A.; Lee, A.; Witt, C. E. *J. Am. Chem. Soc.* **1964**, *86*, 4229.

(13) Lagendijk, A.; Szwarc, M. *J. Am. Chem. Soc.* **1971**, *93*, 5359.

(14) Wilt, J. W.; Maravetz, L. L.; Zawadzki, J. F. *J. Org. Chem.* **1966**, *31*, 3018.

Scheme III



volves longer radical unit combination. Termination probably does not occur via disproportionation since 1-methylnaphthalene was not formed from the initially generated radicals. The products (oligomers and combination products) from benzo-*p*-isotoluene require an out of cage reaction. A second order expression can be derived for the disappearance of benzo-*p*-isotoluene if it is assumed that all radicals present could be represented by R·. It is generally assumed that the reactivity of a given radical is independent of its length in vinyl polymerization; therefore, a single rate constant can characterize all propagation steps occurring in the oligomerization of **5**.

The rate is equal to the sum of initiation and propagation rates.

$$-\frac{d[5]}{dt} = k_i[5]^2 + \frac{k_p k_i^{1/2}[5]^2}{k_t^{1/2}}$$

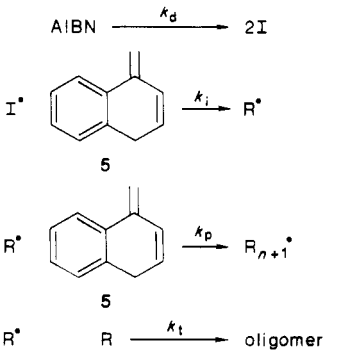
This scheme is in accord with the observed second-order kinetics. The phenomenological rate constant is proportional to $(k_i + k_p k_i^{1/2}/k_t^{1/2})$. In the long-chain approximation, the activation energy E_a is equal to the sum of the energy of propagation E_p and half the energy of initiation if the energy of termination by combination can be assumed to be zero.

Benzo-*p*-isotoluene and AIBN. Benzo-*p*-isotoluene was found to react with AIBN. The product from the reaction of **5** was an oligomer similar to that formed from the self-initiated reaction [H^1 NMR δ 7.0–7.5 (4 H), 5.6–5.9 (1 H), and 2.3–3.2 (5 H); all of the peaks were broad].

The order of the reaction with respect to AIBN was determined to be 0.56 ± 0.03 by observing the effect on the initial rate (under 30% conversion) of maintaining the benzo-*p*-isotoluene concentration constant (1 M in benzene-d_6) while doubling the AIBN concentration (0.085 and 0.17 M). The kinetic chain length of the initiated reaction of benzo-*p*-isotoluene was estimated to be 2.8 from the rate of polymerization of benzo-*p*-isotoluene relative to the rate of initiation by AIBN (calculated from k_d decomposition rate of AIBN[11] and the efficiency of AIBN[12]). Two times the kinetic chain length gives an average molecular chain length of 5.6 if termination is by dimerization.

A possible mechanistic scheme for the initiation of benzo-*p*-isotoluene, **5**, by AIBN can be represented,

Scheme IV



Scheme IV, where the rate of disappearance of benzo-*p*-isotoluene is

$$-\frac{d[5]}{dt} = fk_d[\text{AIBN}] + \left[\frac{fk_d}{k_t}\right]^{1/2} \times k_p[5][\text{AIBN}]^{1/2}$$

Since there was an experimental half-order rate dependence on the concentration of AIBN, it is valid to assume long chain lengths and ignore the first term on the right side of the rate law above.

The significant difference in the fate of *p*-isotoluene, **1**, and benzo-*p*-isotoluene, **5**, might be rationalized by steric effects. The cage recombination process might be slower by a factor of 10 so that addition to the methylene terminus of **5** might occur to a greater extent.

Dibenzo-*p*-isotoluene. Dibenzo-*p*-isotoluene, **8**, was prepared from 9-anthroic acid by the methodology utilized for *p*-isotoluene.

Dibenzo-*p*-isotoluene was purified by column chromatography over neutral alumina eluting with 3:7 chloroform–hexane. After chromatography **8** was recrystallized from pentane to give white needlelike crystals, which melted at 76–77 °C. Nojima reported that dibenzo-*p*-isotoluene melted at 74–75 °C; proton NMR spectral information supplied by Nojima is in agreement with **8** synthesized by the nitrogen oxide elimination route.[9] Compound **8** was not as heat sensitive as compounds **1**, **2**, and **5**; therefore, **8** was stored at 0 °C under nitrogen.

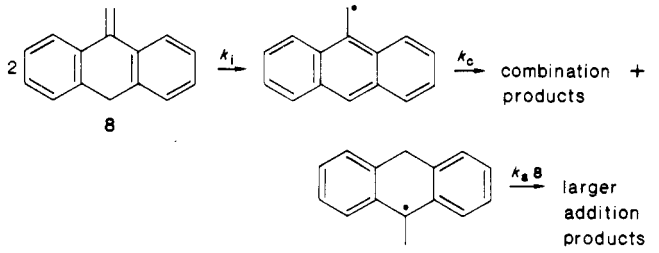
The order of the dibenzo-*p*-isotoluene, **8**, reaction was determined by observing the effect on the initial rate

(under 30% reaction) of varying the concentration of 8 (0.24, 0.48, and 0.96 M at 140 °C).

$$-\frac{d[8]}{dt} = k[8]^n$$

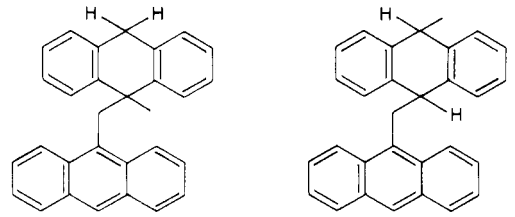
The gradient of a plot of log concentration versus log initial rate gives the reaction order $n = 2.0 \pm 0.1$.

The activation parameters were determined by pyrolysis of 8 at 122, 140, and 160 °C; log k_8 (L/mol s) = $(9.13 \pm 0.05) - (27\,100 \pm 100)/2.3RT$. The energetics for the reaction of dibenzo-*p*-isotoluene especially the frequency factor A ($10^{9.13\pm0.05}$) suggest a nonconcerted reaction again with little orientational demand in the transition state as in the pyrolysis of 1 and 5.



The product was a white precipitate, which was insoluble in benzene. The solubility of the product was tested in other solvents both hot and cold without success (chloroform, methylene chloride, carbon tetrachloride, acetonitrile, dimethyl sulfoxide, tetrachloroethylene, hexachlorobutadiene, 1-methylnaphthalene, cyclohexane, and pentane); therefore, NMR analysis was not possible. The formation of 9-methylanthracene was not observed by NMR (9-methylanthracene is a yellow solid, which is soluble in benzene).

Combination products with the structures **19** and **20**, were not observed.



19 20

Nojima reported both **19** and **20** could be recrystallized from benzene–petroleum ether and both are soluble in chloroform ($CDCl_3$).[9] No part of the product from dibenzo-*p*-isotoluene pyrolysis was soluble in $CDCl_3$ after all of the benzene-d_6 and starting material were removed (no proton NMR signal).

Dibenzo-*p*-isotoluene and Styrene. Dibenzo-*p*-isotoluene (1 M) enhanced the rate of styrene (1 M) polymerization by ca. 4-fold at 140 °C in degassed benzene-d_6. Di-*tert*-butyl peroxide was utilized in an attempt to initiate the dibenzo-*p*-isotoluene reaction. A chain length was estimated by the rate of reaction of dibenzo-*p*-isotoluene (1 M) with added di-*tert*-butyl peroxide (0.2 M) and the rate of di-*tert*-butyl peroxide decomposition;[15] the efficiency of di-*tert*-butyl peroxide is 1.[16] It was calculated that the chain length of the reaction of 8 with di-*tert*-butyl peroxide was ca. unity (0.90).

(15) Log k (/s) = 16–37 000/2.3RT for di-*tert*-butyl peroxide decomposition. Pryor, W. A. *Free Radicals*; McGraw-Hill: New York, 1966.
(16) The standard value of unity is taken for the efficiency of di-*tert*-butyl peroxide. Offenbach, J. A.; Tobolsky, A. V. *J. Am. Chem. Soc.* **1957**, *79*, 278.

Summary

The unimolecular 1,5-hydrogen shift was not observed in any of the 3-methylene-1,4-cyclohexadiene systems studied: *p*-isotoluene, **1**, benzo-*p*-isotoluene, **5**, and dibenzo-*p*-isotoluene, **8**. These materials did participate in radical reactions, but the ultimate fate of the radicals formed from **1**, **5**, and **8** changed from cage recombination and disproportionation with **1** to oligomerization for **5** and perhaps **8**.

o-Isotoluene underwent a concerted ene reaction. The ability to generate an aromatic system directly via the ene reaction probably differentiated it from **1**, **5**, and **8**.

Experimental Section

***N*,*N*-Dimethyl-1,4-dihydrobenzamide.** Anhydrous dimethylamine (5 mL, 0.0756 mol) was dissolved in anhydrous ether (20 mL) under N_2 at 0 °C in a 100-mL round-bottom flask equipped with a dry ice condenser filled with NaCl–water and ice. All openings were protected with drying tubes. 1,4-Dihydrobenzoyl chloride[16] was dissolved in anhydrous ether (10 mL) and slowly added to the stirred dimethylamine–ether solution, which was cooled with a NaCl–water and ice bath. The reaction was stirred for 40 min. The precipitate was filtered, and the ether solution was dried with anhydrous sodium sulfate. The ether was removed under reduced pressure. *N*,*N*-Dimethyl-1,4-dihydrobenzamide was obtained as a thick yellow oil, which was not further purified, 2.295 g (0.015 mol, 92% yield). It was stored under N_2 at 0 °C: NMR (CCl_4) δ 2.4–2.7 (m, 2 H), 2.9–3.0 (s, 6 H), 3.8–4.0 (m, 1 H), 5.4–5.9 (m, 4 H).

***N*,*N*-Dimethyl-1,4-dihydrobenzylamine.** *N*,*N*-Dimethyl-1,4-dihydrobenzamide (2.295 g, 0.015 mol) dissolved in 20 mL of anhydrous ether was added to lithium aluminum hydride (0.994 g, 0.0249 mol) in 20 mL of anhydrous ether under N_2 in a 100-mL three-neck round-bottom flask equipped with condenser and drying tube. After the mixture was heated at reflux for 51 h and cooled to 0 °C, the reaction was quenched with 4 mL of a freshly prepared aqueous anhydrous sodium sulfate solution. The mixture was filtered, and the filtrate was dried over anhydrous sodium sulfate. The ether was removed under reduced pressure. *N*,*N*-Dimethyl-1,4-dihydrobenzylamine, 2.02 g (0.0147 moles, 97% yield), was obtained as a pale yellow oil, which was not further purified: NMR (CCl_4) δ 2.0–2.3 (m, 8 H), 2.5–2.9 (m, 3 H), 5.5–5.7 (s, 4 H). *N*,*N*-Dimethyl-1,4-dihydrobenzylamine was stored under an atmosphere of N_2 at 0 °C.

***N*,*N*-Dimethyl-1,4-dihydrobenzylamine Oxide.** *N*,*N*-Dimethyl-1,4-dihydrobenzylamine (2.020 g, 0.0147 mol) was dissolved in chloroform (75 mL) in a 250-mL Erlenmeyer flask at 0 °C. To this stirred chloroform solution was added *m*-chloroperbenzoic acid (3.658 g, 0.0214 mol) in small portions over a period of 15 min. Anhydrous liquid ammonia was added to quench the reaction until no more *m*-chlorobenzoic acid precipitated. The precipitate was filtered, and the chloroform was evaporated under reduced pressure. *N*,*N*-Dimethyl-1,4-dihydrobenzylamine oxide was obtained as a pale yellow oil, which was not purified further.

3-Methylene-1,4-cyclohexadiene (*p*-Isotoluene). The *N*,*N*-dimethyl-1,4-dihydrobenzylamine oxide was pyrolyzed at 50–100 °C under 30 mm of pressure. The distillate, which was collected in a dry ice trap, contained 3-methylene-1,4-cyclohexadiene and toluene in a 7:1 ratio along with chloroform and dimethylhydroxylamine. Pentane was added, and this solution was washed at 0 °C with 5% hydrochloric acid and then with saturated aqueous sodium bicarbonate to remove the dimethylhydroxylamine. 3-Methylene-1,4-cyclohexadiene was separated from toluene and chloroform by preparative gas chromatography on a 5 ft × $^1/_4$ in. copper column packed with 15% DBTCP on 60/80 chrom P conditioned at 150 °C (injector 115 °C, detector 125 °C, and column temperature 60 °C): NMR (CCl_4) (3-methylene-1,4-cyclohexadiene) δ 2.5 (br s, 2 H), 4.4–4.7 (s, 2 H), 5.4–5.8 (m, 2 H), 5.8–6.2 (d, J = 9 Hz, 2 H).

1,4-Dihydronaphthoic Acid. 1,4-Dihydronaphthoic acid was prepared from 1-naphthoic acid by the method described for the preparation of 1,4-dihydrobenzoic acid.[17] The only difference

(17) Kuehne, M. E.; Lambert, B. F. *Org. Synth.* **1963**, *43*, 22.

was that the consumption of sodium was indicated by the disappearance of a green color. The ether solution was concentrated at room temperature, which yielded a light brown solid, mp 73–76 °C. The solid was recrystallized three times from 40–60 °C petroleum ether to give pure 1,4-dihydronaphthoic acid (65%): mp 85–87 °C (lit.[17] mp 86 °C); NMR ($CDCl_3$) δ 3.4–3.6 (m, 2 H), 4.5–4.7 (m, 1 H), 6.0–6.4 (m, 2 H), 7.1–7.5 (m, 4 H), 12.1 (s, 1 H).

***N,N*-Dimethyl-1,4-dihydronaphthamide.** *N,N*-Dimethyl-1,4-dihydronaphthamide was prepared from 1,4-dihydronaphthoyl chloride by the method described for the preparation of *N,N*-dimethyl-1,4-dihydrobenzamide from 1,4-dihydrobenzoyl chloride described above (95% yield): NMR ($CDCl_3$) δ 2.9–3.1 (s, 6 H), 3.4–3.6 (m, 2 H), 4.6–4.9 (m, 1 H), 5.9–6.2 (m, 2 H), 7.0–7.6 (m, 4 H).

***N,N*-Dimethyl-*N*-(1,4-dihydronaphthyl-1-methyl)amine.** *N,N*-Dimethyl-1,4-dihydronaphthamide was reduced with lithium aluminum hydride to the corresponding amine in a manner described for the preparation of *N,N*-dimethyl-1,4-dihydrobenzylamine (90% yield): NMR ($CDCl_3$) δ 2.3–2.8 (m, 8 H), 3.4–3.9 (m, 3 H), 6.0–6.5 (m, 2 H), 7.0–7.9 (m, 4 H).

***N,N*-Dimethyl-*N*-(1,4-dihydronaphthyl-1-methyl)amine Oxide.** *N,N*-Dimethyl-*N*-(1,4-dihydronaphthyl-1-methyl)amine oxide was prepared from its corresponding amine in a manner described for the preparation of *N,N*-dimethyl-1,4-dihydrobenzylamine oxide.

1-Methylene-1,4-dihydronaphthalene (Benzo-*p*-isotoluene). The *N,N*-dimethyl-*N*-(1,4-dihydronaphthyl-1-methyl)amine oxide was pyrolyzed at 85–105 °C under 0.5 mm of pressure. The distillate contained 1-methylnaphthalene (5%) and benzo-*p*-isotoluene (95%), along with chloroform and dimethylhydroxylamine. The dimethylhydroxylamine was removed by the acid–base wash as described for *p*-isotoluene. The chloroform was removed by bubbling nitrogen through the solution: NMR (benzene-d_6) δ 3.1–3.4 (br s, 2 H), 4.9–5.0 (s, 1 H), 5.5–5.8 (m, 2 H), 6.3–6.5 (d, J = 9 Hz, of t, J = 1.5 Hz, 1 H), 6.8–7.3 (m, 3 H), 7.5–7.8 (m, 1 H).

9,10-Dihydro-9-anthroic Acid. 9-Anthroic acid was reduced in the same manner as described above for benzoic acid to yield 9,10-dihydro-9-anthroic acid, which was recrystallized twice from 95% ethanol to produce white needles in a 83% yield: mp 198–200 °C; NMR (acetone-d_6) δ 3.9 (d, J = 15 Hz, 1 H), 4.35 (d, J = 15 Hz, 1 H), 5.05 (s, 1 H), 7.2–7.6 (m, 8 H), 12.5 (s, 1 H).

9,10-Dihydro-9-anthroyl Chloride. 9,10-Dihydro-9-anthroic acid (4.2 g) was converted to its acid chloride in a manner previously described for conversion of 1,4-dihydrobenzoic acid to its acid chloride.

***N,N*-Dimethyl-9,10-dihydro-9-anthramide.** *N,N*-Dimethyl-9,10-dihydro-9-anthramide was prepared from 9,10-dihydro-9-anthroyl chloride in a manner previously described for conversion of 1,4-dihydrobenzoyl chloride to *N,N*-dimethyl-1,4-dihydrobenzamide. The only difference was that the precipitate formed after reaction was filtered hot to keep the amide in the ether solution. Removal of the ether gave a solid *N,N*-dimethyl-9,10-dihydro-9-anthramide, which was recrystallized once from anhydrous ether to produce white cubic crystals in a 85% yield: NMR (acetone-d_6) δ 2.65–3.5 (2 broad peaks, 6 H), 3.8 (d, J = 16 Hz, 1 H), 4.55 (d, J = 16 Hz, 1 H), 5.5 (s, 1 H), 7.1–7.5 (m, 8 H).

(18) Auwers, K. Von; Möller, K. *J. Prakt. Chem.* **1925**, *109*, 124.

***N,N*-Dimethyl-*N*-(9,10-dihydroanthryl-9-methyl)amine.** *N,N*-Dimethyl-9,10-dihydro-9-anthramide was reduced to its amine in a manner previously described for the reduction of *N,N*-dimethyl-1,4-dihydrobenzamide with the exception that the amide was added to the lithium aluminum hydride–ether solution as a solid. The mixture formed after workup was filtered hot to keep the amine in solution. *N,N*-Dimethyl-*N*-(9,10-dihydroanthryl-9-methyl)amine was obtained as a light yellow solid: NMR ($CDCl_3$): δ 2.1 (s, 6 H); δ 2.4 (d, J = 8 Hz, 2 H); δ 3.5–3.7 (m, 1 H); δ 3.9–4.3 (m, 2 H); δ 7.1–7.5 (m, 8 H).

***N,N*-Dimethyl-*N*-(9,10-dihydroanthryl-9-methyl)amine Oxide.** The procedure followed was that described for the preparation of *N,N*-dimethyl-1,4-dihydrobenzylamine oxide, except that the *N,N*-dimethyl-*N*-(9,10-dihydroanthyl-9-methyl)-amine was oxidized in methylene chloride. *N,N*-Dimethyl-*N*-(9,10-dihdyroanthryl-9-methyl)amine oxide was obtained as a light yellow solid, which was not purified further.

9-Methylene-9,10-dihydroanthracene (Dibenzo-*p*-isotoluene). The *N,N*-dimethyl-*N*-(9,10-dihydroanthryl-9-methyl)amine oxide was pyrolyzed at 80 °C under 0.1 mm of pressure for 30 min. A yellow solid remained in the distillation flask, which contained 9-methylene-9,10-dihydroanthracene (80%) and 9-methylanthracene (20%). The yellow solid was dissolved in 30% $CHCl_3$–70% hexane and chromatographed on a neutral alumina column. 9-Methylene-9,10-dihydroanthracene (white solid) was the first to be eluted followed by 9-methylanthracene (yellow solid). The 9-methylene-9,10-dihydranthracene was recrystallized from pentane to give white needlelike crystals (overall yield of pure material 30%): mp 76–77 °C (lit.[q] mp 74–75 °C); NMR (benzene-d_6) δ 3.7 (s, 2 H), 5.55 (s, 2 H), 6.9–7.2 (m, 6 H), 7.5–7.8 (m, 2 H).

Kinetic Experiments. A typical kinetic run consisted of introducing a benzene-d_6 solution of **1**, **2**, **5**, or **8** (ca. 1 M *p*-isotoluene, benzo-*p*-isotoluene, or dibenzo-*p*-isotoluene; ca. 0.5 M *o*-isotoluene) in a NMR tube, which was treated by washing with acetone, deionized water, and dilute ammonium hydroxide. The NMR tubes were dried in an oven overnight. The benzene solution was degassed through three freeze–thaw cycles and sealed under vacuum. The kinetics were monitored by ^1H NMR (90 MHz) spectroscopy by observing the disappearance of the exocyclic methylene protons (no products formed in that region) as a function of time. An internal standard (tetramethylsilane) was used in the pyrolysis of benzo-*p*-isotoluene and dibenzo-*p*-isotoluene. No internal standard was used with *o*-isotoluene and *p*-isotoluene because it was possible to integrate over all protons (both starting material and products). Five integrations were averaged to obtain a percent reaction at percent given time interval. All errors denoted for compounds **1**, **2**, **5**, and **8** are average deviations obtained from two separate experimental runs, i.e. for determination of activation parameters and reaction orders. Constant temperature baths were obtained by refluxing pure solvents with various boiling points [36 °C *n*-pentane, 58 °C acetone, 82 °C cyclohexane, 100.5 °C deionized water, 122 °C tetrachloroethylene, 140 °C *m*-xylene, 160 °C bis(2-methoxyethyl) ether]. A refrigerated water bath was used to obtain temperatures of 10 °C and 21 °C. Temperatures were constant to (±0.5 °C) throughout the kinetic run.

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