Experimental Section[10]

1-Fluoro-2-methylnaphthalene (5). Diazotization of 1-amino-2-methylnaphthalene[11] and conversion into the diazonium hexafluorophosphate were carried out as described.[9] Pyrolysis at 170–180 °C in mineral oil for 30 min afforded crude **5**, which on redistillation afforded 63% of twice distilled **5**, bp 62 °C at 0.5 mm.[8]

Reaction of 5 with Benzalaniline (4). A mixture of 1.6 g of **5**, 1.8 g of **4**, 2.8 g of *t*-BuOK, and 15 mL of DMF was heated at 95 ± 3 °C for 90 min, cooled, and added to 150 mL of 10% HCl. The organic product, isolated as usual, was dissolved in 20 mL of ethanol. On cooling, a colorless solid separated and was recrystallized from benzene–petroleum ether (30–60 °C) to yield 420 mg (18%) of **7**, mp 167–168 °C: MS *m/e* 321;[12] NMR [$(CH_3)_4Si$, $CHCl_3$] δ 5.65 (s, 1, NH, exchanged by D_2O), 6.51–8.18 (m, 18, ArH, CH=CH). Further crystallization of the material in the mother liquor from benzene–petroleum ether (30–60 °C) afforded 100 mg (3%) of colorless **6**, mp 164–165 °C, giving blue fluorescence in benzene: MS *m/e* 321; NMR 2.98 (q, 1, J_{ac}, −4 Hz, J_{bc} = −15 Hz), 4.06 (q, 1, J_{ab} = −10 Hz, J_{bc} = −15 Hz), 5.15 (q, 1, J_{ac} = −4 Hz, J_{ab} = −10 Hz), 6.78–7.95 (m, 16, ArH). Anal. Calcd for $C_{24}H_{19}N$: C, 89.7; H, 5.9; N, 4.4. Found: C, 90.2; H, 5.9; N, 4.0.

Alkaline extraction of the material remaining in the mother liquor followed by acidification of the extract and crystallization from benzene–petroleum ether (30–60 °) afforded 200 mg (7%) of **8**: mp 150.5–151.5 °C; MS *m/e* 246;[12] NMR 5.56 (s, 1, OH exchangeable with D_2O), 6.90–8.23 (m, 13 H, ArH, CH=CH). Anal. Calcd for $C_{18}H_{14}O$: C, 87.8; H, 5.7. Found: C, 88.2; H, 5.8.

After heating a solution of 0.25 g of **1**, prepared as described[3] with 0.09 g of aniline and 1.1 g of *t*-BuOK in 10 mL of DMF for 12 h at 100–110 °C, most (85%) of the **1** was recovered, and no trace of **6** or **7** was found using TLC (neutral alumina).

***trans*-1-(1-Bromo-2-naphthyl)-2-phenylethylene (9).** A mixture of 4.4 g of 1-bromo-2-methylnaphthalne,[11] 3.6 g of **4**, 4.5 g of *t*-BuOK, and 80 mL of DMF was heated at 95 °C for 1 h, cooled, and poured into 120 mL of 10% HCl. On crystallization from ethanol of the organic products, isolated as usual, there was obtained 3.6 g (58%) of **9**: mp 115–116 °C (lit.[13] mp 121–122 °C); MS *m/e* 308, 310.[12]

1-(*o*-Fluorophenyl)-2-phenylethylene (10). In a Siegrist reaction similar to those described above (1 h at 95 °C), *o*-fluorotoluene was converted in 28% yield into **10**: mp 103.0–103.5 °C, MS *m/e* 198.[12] Anal. Calcd for $C_{14}H_{11}F$: C, 84.8; H, 5.6; F, 9.6. Found: C, 84.7, H, 5.5; F, 9.6.

The mother liquor on evaporating to dryness gave an impure oil (several spots on TLC) containing nitrogen but no fluorine on elemental analysis. No further attempt was made to purify it.

Registry No.—**4**, 538-51-2; **5**, 573-99-9; **6**, 64345-68-2; **7**, 64345-71-7; **8**, 64345-70-6; **9**, 27854-69-9; **10**, 64345-69-3; 1-bromo-2-methylnaphthalene, 2586-62-1; *o*-fluorotoluene, 95-52-3.

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(1) This research was supported by Research Grant CA-07394 from the National Cancer Institute, Department of Health, Education, and Welfare.
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(10) All melting and boiling points are uncorrected. Microanalyses were performed by M-H-W Laboratories, Gardon City, Mich. The phrase "worked up as usual" means that an ether–benzene solution of the reaction products was washed successively with dilute acid and/or alkali and saturated NaCl, and dried by passing through a cone of anhydrous $MgSO_4$. The solvent was then removed on a rotary evaporator and the product treated as described.
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(12) Mass spectra were determined by C. R. Weisenberger on an MS 9 instrument made by A.E.I.
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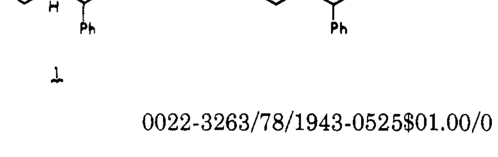
Communications

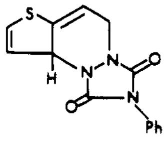
Thermal Reaction between 5-Methylene-1,3-cyclohexadiene and Styrene[1]

Summary: At 80 °C 5-methylene-1,3-cyclohexadiene reacts rapidly, $t_{1/2} \sim 6$ min, with styrene to produce a 3:1 mixture of 1,2- and 1,3-diphenylpropane in 90% yield. The triene does not initiate the polymerization of styrene.

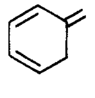
Sir: The proposal[2] that the monoradical forming step in the thermal polymerization of styrene involves hydrogen atom transfer from a preformed dimer **1** to styrene (Scheme I) has received considerable support.[3] Isolation of **1** has not been accomplished yet, but an analogue **2** has been prepared and shown to initiate the polymerization of styrene.[4]

Scheme I





2



3

In another attempt to verify some of the chemistry attributed to **1** the corresponding parent triene, 5-methylene-1,3-cyclohexadiene (**3**), has been prepared and some of its reactions studied. The preparation of **3** by thermolysis of an ester has been reported already.[5] The search for a compound that might decompose at a much lower temperature and allow **3** to be generated slowly in styrene solution led to the alternate synthesis shown in Scheme II. Itaconic anhydride and α-pyrone were heated under N_2 in toluene at 90 °C for 65 h to

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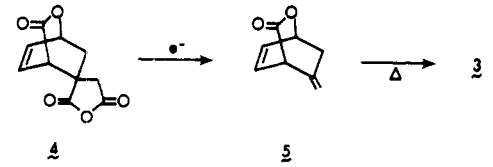
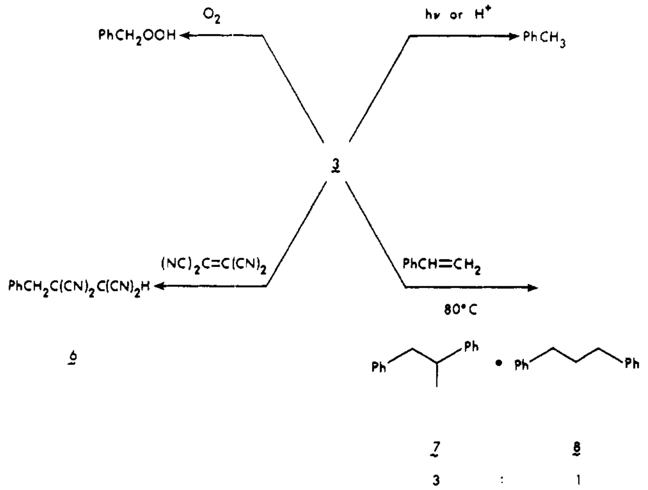
Scheme II



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

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(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]

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(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 ^{1}H NMR. First-order kinetics were obtained over at least 3 half-lives.

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(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 ^{1}H 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]

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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