Tetrahedron Vol. 42, No. 22, pp. 6189 to 6194, 1986
Printed in Great Britain.

0040-4020/86 $3.00+.00
Pergamon Journals Ltd.

THE DIENE COMPONENT IN THE CATION RADICAL DIELS–ALDER

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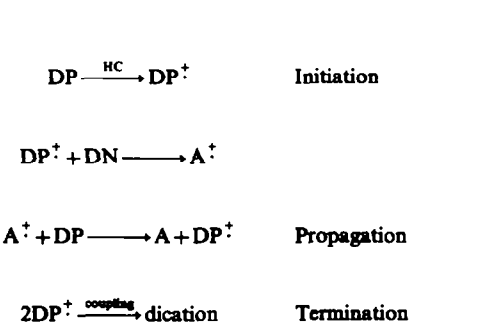
(*Received in U.S.A.* 4 *October* 1985)

Abstract—The scope of and structural constraints upon the diene component in the cation radical Diels–Alder are investigated, with special attention to electronic, steric, and conformational effects. The major factors which control the competition between Diels–Alder and cyclobutane adduct formation are also illustrated.

The cation radical (or hole-catalyzed) Diels–Alder cycloaddition reaction offers a format for rapid, stereospecifc, and stereoselective addition of ionizable dienophiles to conjugated dienes.[1-3] Mechanistically, the reaction is a cation radical chain process initiated by a hole (i.e. single electron acceptor) catalyst or by ionizing radiation and consisting of alternating cycloaddition and electron transfer propagation steps (Scheme 1). In effect, hole catalysis provides a means of effecting cycloadditions in the domain of cation radicals, where activation energies typically are minimal in comparison to those for cycloadditions of neutrals. When this cation radical cycloaddition step is coupled with electron transfer from one of the participating addends to the adduct cation radical, a chain process is set up which yields the neutral adduct molecule and re-cycles the catalyzing "hole". Theoretical calculations and considerations, as well as previous experimental observations, suggest that normally the ionized component preferentially adopts the dienophilic role where feasible.[1,4,5] In this way, conjugated or electron-rich π substrates, which are relatively readily ionized, can be effectively utilized as Diels–Alder dienophiles, despite the fact that such substrates could not ordinarily be induced to participate effectively in the neutral Diels–Alder. In like manner, a high degree of alkyl substitution in such a conjugated or electron-rich substrate, which would easily be sufficient to preclude the neutral Diels–Alder, as a consequence of steric repulsion,[6] quite often results in enhancement of Diels–Alder adduct formation as a consequence of the increased ease of ionization and decreased rate of termination, the latter usually involving the coupling of two cation radicals. As a consequence of these and other related considerations, it is apparent that the dienic component in a crossed cation radical Diels–Alder reaction is normally the less ionizable component. It was the purpose of this investigation to define in detail the generality of dienic participation in the cation radical Diels–Alder and the factors which influence dienic aptitude in this reaction. Special emphasis was placed on conformational effects, the effect of the degree and position of alkyl and heteroatomic group substitution, and the potential competition between Diels–Alder and cyclobutane adduct formation.

In addition to the constraint that the dienic component be less readily ionizable than the dienophilic component, the generality of the dienic role is further limited by the incompatibility of certain functional groups with the highly reactive chain-carrying cation radicals involved in the propagation steps of the reaction. As a consequence of the electrophilicity of organic π cation radicals, the presence of nucleophiles which can react irreversibly with (scavenge) the chain-carrying species, either in the medium or on one of the reaction components, strongly retards or quenches the chain process. An excellent example is the quenching of the cation radical dimerization of 1,3-cyclohexadiene by isopropyl alcohol and by triethylamine.[7,8] Cation radicals possessing β hydrogens are known to be strong Bronsted acids and are therefore also susceptible to quenching through deprotonation by bases.[9] Finally, the tendency of cation radicals to undergo single electron transfer makes quenching by irreversible electron transfer highly probable when readily ionizable groups (amines, sulfides, etc.) are present in the medium or on either reaction component, except when conjugated with one of the reactant π systems.† In the latter case, the ionizability of the reaction partner having the conjugated donor substituent is usually enhanced so greatly that this compound is exclusively ionized and participates as dienophile, if at all. Conjugated amino substituents, in fact, appear to provide such extensive



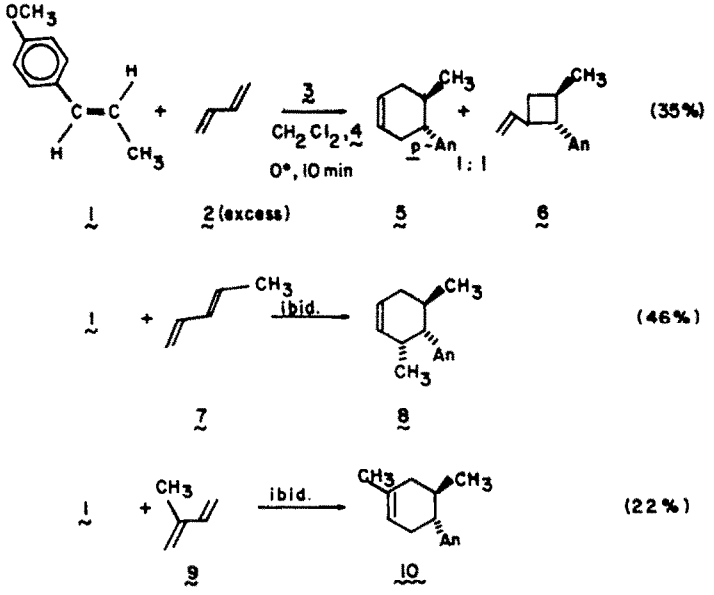
Scheme 1. Mechanism of the cation radical chain Diels–Alder (HC, hole catalyst; DP, dienophile; Dn, diene; A, adduct).

† The cation radical Diels–Alder is strongly retarded by added triarylamine.[10]

stabilization to the cation radical that even dienophilic participation is normally precluded. Multiple electron donating oxygen or sulfur-containing substituents produce the same effect.[11] On the other hand, the presence of even mildly electron-withdrawing substituents on either reactant is often sufficient to suppress the cation radical chain mechanism. When present on the dienophile, particularly in a conjugated relationship, such substituents suppress ionization. Further, since cation radical reactivity is predominantly electrophilic, electron-deficient dienes also make very poor dienic components. As a consequence of all of these considerations, the most effective dienic components are those which have neither powerfully electron-donating nor electron-withdrawing substituents. Cyclic dienes such as 1,3-cyclohexadiene and 1-methyl-1,3-cyclohexadiene have received the most attention as dienic components in the early phases of the research on the cation radical Diels–Alder, although several examples of participation of acyclic dienes in this role were noted.[1-5] One of the objectives of the present work was to define more fully the aptitude of simple acyclic dienes for this role. A common dienophile, t-anethole (1) was selected for the entire range of acyclic dienes studied. This substrate is relatively easily ionized and thus is well suited for the dienophilic role vs a range of conjugated dienes of varying ionizability. Lacking a true diene system, 1 is unable to function in the dienic role, thus assuring that the 1^+ produced cannot participate in the alternate, dienic, role.

RESULTS AND DISCUSSION

Cation radical cycloadditions of the parent conjugated diene (1,3-butadiene, 2) have not previously been reported, and it was of considerable interest to ascertain whether this simplest diene could participate in the cation radical Diels–Alder. The standard reaction conditions, applied to all of the dienes included in this study except where noted, consisted of adding a catalyst/initiator solution consisting of 50 mol% (based upon 1) of tris-(*p*-bromophenyl)aminium hexachloroantimonate (3) dissolved in dichloromethane to a dichloromethane solution of t-anethole (1), the appropriate dienic component, and 2,6-di-t-butylpyridine (4) in the molar ratios 1:1:0.6 at 0° and quenching the reaction by addition of excess methoxide/methanol solution after 10 min reaction time. The hindered amine was included to assure the absence of Bronsted acid-catalyzed reactions,[12,13] which are an occasional concomitant of aminium salt-initiated cation radical reactions. In the reactions of this study, the hindered amine actually had no significant effect on the nature of the cycloaddition products or their relative amounts. The relatively large quantity of aminium salt required in the hindered amine-modified procedure is a consequence of extensive decomposition of this salt by the amine. Reaction conditions were not optimized, and it is possible that use of still larger amounts of the aminium salt would produce higher yields. In any case, the products reported herein are the only non-volatile (non-polymeric) products formed except for the cyclodimers of the reactants (t-anethole and the various dienes). The stability of the cycloadducts under the reaction conditions and the correspondence of the products to those obtained in the photosensitized electron transfer (PET) version of the reaction were established in most instances. In contrast to most of the reaction studies, butadiene yielded only traces of cycloaddition products under the standard reaction conditions. However, use of a massive excess of the diene gave a modest yield (35%, isolated) of the two cycloadducts. In further contrast to virtually all previously reported cation radical cycloadditions involving dienophiles of the styrene (e.g. 1) or the conjugated diene type, this cycloaddition reveals competition between cyclobutane (CB) and Diels–Alder (DA) adduct formation (1:1 ratio of 5:6; Scheme 2). Thus the low reactivity of butadiene

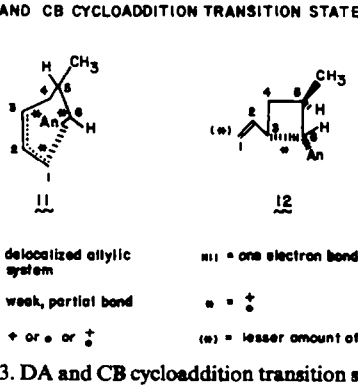


Scheme 2.

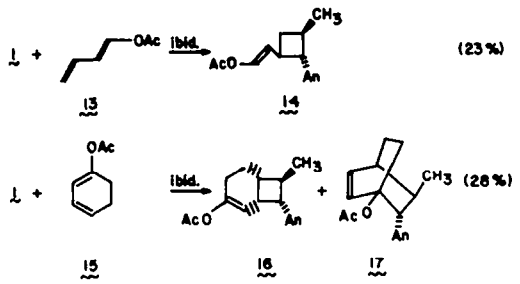
toward 1^+ is accompanied by a loss of DA selectivity. In part, both of these effects may be engendered by the relatively low proportion of the *s-cis* conformer of **2** which is required for DA addition, but the contrasting results obtained with 1,3-pentadiene (**7**) suggest an additional factor. The latter diene, even under the standard reaction conditions, affords a 46% (unoptimized) yield of a single cycloadduct, the DA adduct **8** (Scheme 2). The major rate-enhancing effect of a terminal methyl substituent, specifically on the DA cycloaddition, is graphically illustrated in the contrasting reactivities of **7** and **2**, and the selectivity of the former. Inspection of reasonable transition state models for the CB (**11**) and DA (**12**) cycloaddition (Scheme 3) illustrate the expectation that a greater positive charge accumulation on the terminal diene carbon (C_1) is expected in the DA transition state, which should therefore be more susceptible to stabilization by terminal alkyl groups. The obtention of a single DA adduct also reflects the exceptional *endo* selectivity quite often encountered in the cation radical Diels–Alder.[1-5]

Under the standard conditions, isoprene (**9**) also affords a single Diels–Alder adduct **10** (22% yield, Scheme 2), revealing that methyl substitution at an internal (2- or 3-) position of the diene system also returns to normal DA selectivity. Conventional VB structures for the cation radical cycloaddition transition states (**11**, **12**) suggest that methyl substitution at this position should enhance the rates of both DA and CB cycloaddition, but selective enhancement of DA cycloaddition is not necessarily expected. It appears likely that the primary factor which allows the DA cycloaddition to reassert its customary predominance here is the enhancement of the *s-cis* conformer population characteristics of this diene substitution pattern, or more precisely, the unreactivity of these *s-cis* isomers engendered by the same effects which de-stabilize the *s-cis* conformer thermodynamically.

In significant contrast to the results with *E*-1,3-pentadiene and 1,3-butadiene, *E*-1-acetoxy-1,3-butadiene (**13**) yields only the cyclobutane adduct **14** (Scheme 4).[14] In terms of the previous theoretical framework, the implication appears to be that the acetoxy group is mildly electron withdrawing and thus discourages the DA cycloaddition more than the CB cycloaddition. Support for this somewhat surprising proposal comes from the observation that 1-acetoxy-



Scheme 3. DA and CB cycloaddition transition state models.

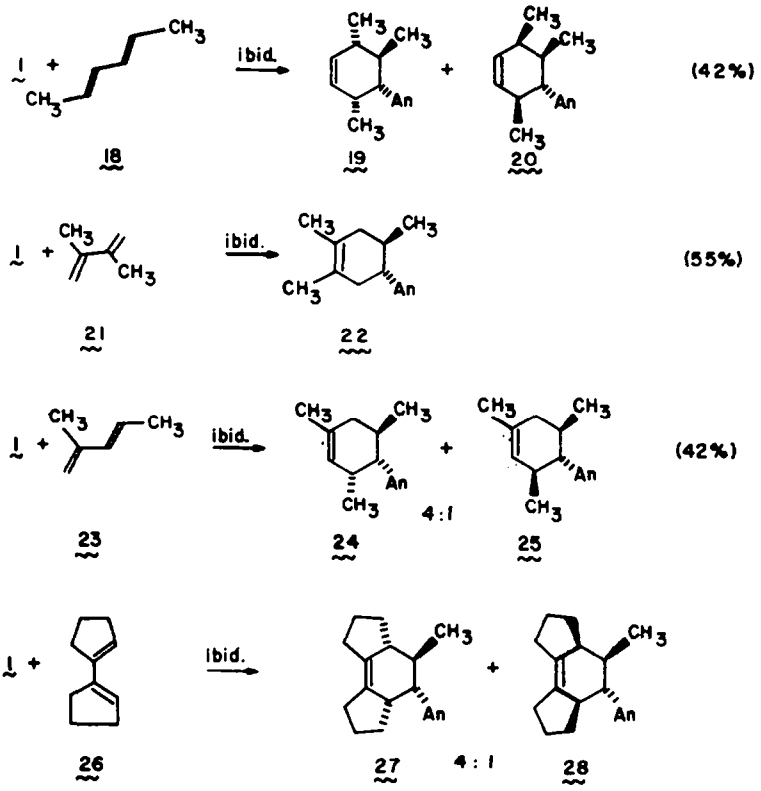


Scheme 4.

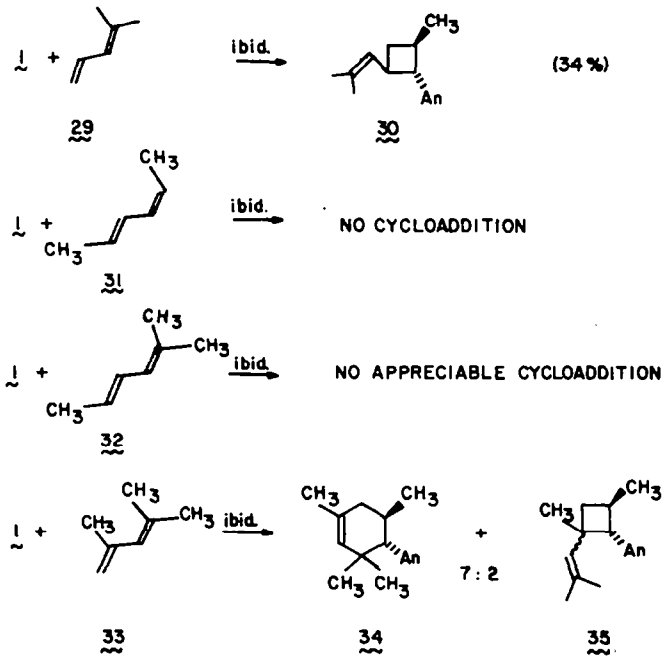
1,3-cyclohexadiene is completely unreactive toward the aminium salt **4**, whereas 1,3-cyclohexadiene and, even more, 1-methyl-1,3-cyclohexadiene are dimerized extremely rapidly in the presence of 3–5 mol% of **4**. Apparently, the terminal acetoxy function elevates the ionization potential of the diene, i.e. it destabilizes the cation radical relative to the neutral. Though admittedly surprising in the context of substituent constants and of carbocation reactions such as electrophilic aromatic substitution, destabilization by the acetoxy group appears to be a general and noteworthy feature of cation radical cycloaddition chemistry.

The fact that both terminal and internal alkyl substituents on a conjugated diene favor DA cycloaddition suggests that the latter cycloaddition mode should predominate with a wide variety of acyclic dienes. This surmize is borne out by studies (Scheme 5) with *E,E*-2,4-hexadiene (**18**), 2,3-dimethyl-1,3-butadiene (**21**), *E*-2-methyl-1,3-pentadiene (**23**), and 1,1′-dicyclopentenyl (**26**), all of which yield DA adducts exclusively.

The preceding inventory of dienes is characterized by the absence of a terminal *Z* (i.e. *cis*) substituent, a structural feature which, when present, is associated with notoriously low DA dienic activity.[6] Indeed, this characteristics behavior extends to the cation radical DA, once again permitting CB cycloaddition to become dominant (Scheme 6). In the specific case of 2,4-dimethyl-1,3-pentadiene (**33**), where the 2-alkyl substituent effect (favoring DA cycloaddition) is counterpoised against the terminal *Z* substituent effect (favoring CB cycloaddition), a mixture of DA and CB cycloadditions is observed (**34**, **35**). It is of interest that whereas a terminal *Z* substituent normally effectively eliminates DA cycloaddition, CB cycloaddition is not adversely affected. This suggests that CB cycloaddition, unlike DA addition, does not require the *s-cis* diene conformer, which is so strongly disfavored by a *Z* substituent, but instead proceeds via the more abundant *s-trans* conformer. However, if an additional substituent is added at the other terminus, both cycloaddition modes are suppressed (**31**, **32**) (Scheme 6). It will be recalled (see **18**, Scheme 5) that DA cycloaddition is not adversely affected by such a second terminal substituent. Evidently the CB cycloaddition is far more sensitive to steric effects at that terminal diene position undergoing primary bond formation in the highly non-synchronous CB cycloaddition than in the relatively more synchronous DA addition. The validity of this steric rationale is further supported by the observation that 4-vinylanisole, which lacks the β-methyl substituent of **1**, adds



Scheme 5.



Scheme 6.

smoothly to *E*-2-methyl-2,4-hexadiene (**32**), to give a cyclobutane adduct, in contrast to the unreactivity of **1** toward this same diene.

These observations not only facilitate the development of synthetic strategies to favor either DA or CB cycloaddition, as may be desired, but also strongly suggest that mechanistically the two cycloaddition paths (DA and CB) are quite discrete, not sharing a common bond initiation step or a common acyclic, open cation/radical intermediate, in excellent accord with theory.

EXPERIMENTAL

Instrumentation. Routine ^{1}H- and ^{13}C-NMR spectra were recorded on Varian EM 390 and FT-80A spectrometers, respectively. All samples were dissolved in $CDCl_3$. All chemical shifts and coupling constants (J) are reported in ppm (relative to a TMS reference) and hertz, respectively. ^{1}H-NMR data are reported as follows: chemical shift (multiplicity, integration, coupling constant). Gas chromatographic (GC) analyses were performed with a Gowmac series 550P instrument equipped with a thermal conductivity detector and a 4 ft × 1/8 in. stainless steel column packed with OV-1 on Chromosorb P (AW, DMCS, 80–100 mesh) in conjunction with a Hewlett–Packard 3390A integrator. Gas chromatograph–mass spectra (GCMS) data were recorded with a Finnigan 4023 mass spectrometer with a 50 m DB-1 (0.25 μm film) capillary column and are presented as *m/e* (% rel. intensity). The GC and GCMS analyses were performed with helium as the carrier gas. High resolution mass spectra were obtained with a Dupont (CEC) 21-110 mass spectrometer.

Chemicals, materials and techniques. Unless otherwise noted, chemicals were obtained from Aldrich Chemical Co., Milwaukee, WI and were used without further purification. Reactions were carried out in dry dichloromethane (DCM; distilled from P_2O_5). Tris(4-bromophenyl)aminium hexachloroantimonate (aminium salt) was washed thoroughly with anhyd ether and then dried *in vacuo* prior to use. Typically, a 50 mol% (relative to the limiting reagent—usually *trans*-anethole, **1**, or 4-vinylanisole) DCM soln of the aminium salt was added via syringe as rapidly as possible to a cooled (0°), magnetically stirred DCM soln containing 60 mol% 2,6-di-t-butylpyridine (DTBP) and an appropriate ratio of some hydrocarbon diene to **1** or 4-vinylanisole. Usually after no more than 10 min, the reaction was quenched by the addition of a sat methanolic soln of K_2CO_3 (the quenched mixture was typically pale yellow in contrast to the blue color associated with some cation radicals and the aminium salt). The resulting mixture was then diluted with pentane (3–4 volumes), filtered, washed with water then brine, dried by passing the soln through cotton, and concentrated on a rotary evaporator. The residue was decanted from any precipitated tris(4-bromophenyl)amine (TBPA) and was then purified by either column chromatography (silica gel, 60–200 mesh) or thick layer chromatography (silica gel, 2000 μm; Analtech) often followed by distillation. With the usual 5:1 Skelly B/benzene solvent system, the order of elution during chromatographic separations was TBPA, DTBP, hydrocarbon dienes and cross adducts, cross adducts from **1** or 4-vinylanisole and hydrocarbon dienes, dimers of **1** or 4-vinylanisole, then unidentified oligomers (major by-products).

Synthesis of 3,5-*dimethyl*-4-(4′-*methoxyphenyl*)*cyclohexene* (**8**)

General procedure. To an oven dried 25 ml round bottom flask equipped with a magnetic stir bar was added 193.4 mg (1.305 mmol) of **1**, 439.5 mg (6.452 mmol) of *trans*-piperylene, and 151.5 mg (0.74 mmol) DTBP in 6 ml of DCM. After cooling the stirred soln to 0°, 512.4 mg (0.63 mmol) of the aminium salt partially dissolved in 6 ml of DCM were added via syringe as rapidly as possible. After 10 min, aliquots of a sat methanolic K_2CO_3 soln were added until a light amber color persisted. The crude mixture was transferred to a clean flask, diluted with 75 ml of pentane, and allowed to stand until all the TBPA had precipitated (*ca* 5 m). The soln was filtered into a separatory funnel and washed with an equal volume of brine. The aqueous wash was extracted with 2 × 50 ml portions of pentane. The combined extracts were filtered through cotton and then concentrated with a rotary evaporator. To the crude product was added 4–5 ml of pentane, thereby precipitating more TBPA. The liquor was then decanted and the remaining solid washed with 2 × 5 ml portions of pentane. The combined liquor and washes were concentrated to a volume of 3 ml. Thick layer chromatography facilitated the isolation of crude product (R_f = 0.4) which still contained small amounts of TBPA (^{1}H-NMR). Distillation (125–130°, 1 Torr) afforded 130.3 mg (0.602 mmol, 42%) of **8** as a clear colorless oil: GCMS showed two peaks in a 10:1 ratio having identical mass spectra: 216 (M^+), 148 (100); ^{1}H-NMR δ 0.7 (d, 3H, 6), 0.76 (d, 3H, 6), 1.50–1.95 (m, 1H), 1.98–2.50 (m, 3H), 2.5–2.8 (dd, 1H), 3.72 (s, 3H), 5.68 (bs, 2H), 6.79 (d, 2H, 9), 7.17 (d, 2H, 9); ^{13}C-NMR δ (major isomer) 16.82, 20.58, 26.59, 34.80, 35.57, 50.59, 55.14, 113.31 (2C), 125.12, 130.12 (2C), 133.51, 135.46, 157.73; calc for $C_{15}H_{20}O$: 216.151406; meas: 216.150682.

Synthesis of 4-(4′-*methoxyphenyl*)-5-*methylcyclohexene* (**5**) *and* 1-*ethenyl*-2-(4′-*methoxyphenyl*)-3-*methylcyclobutane* (**6**)

The general procedure was followed except that DTBP was omitted. In addition, only 21.6 mol% of the aminium salt and a large excess of 1,3-butadiene (Pfaltz and Bauer, 99%), *ca* 7 ml (condensed at −30°), were used. Column chromatography followed by distillation (90–120°, 1 Torr) afforded 4048 mg (2.00 mmol, 35.2%) of a clear, colorless, viscous oil which was a 1:1 mixture of two components (GC): GCMS showed that the two peaks had identical mass spectra except for the intensities of the parent ions: cyclohexene: 202 (M^+), 148 (100), cyclobutane: 202 (M^+), 148 (100); ^{1}H-NMR δ (**5**) 0.7 (d, 3H, 6), 1.2–1.63 (m, 1H), 2.22 (m, 4H), 2.67 (m, 1H), 3.75 (s, 3H), 5.72 (s, 2H), 6.85 (d, 2H, 9), 7.13 (d, 2H, 9); (**6**) 1.12 (d, 3H, 6), 1.95 (m, 3H), 2.22 (m, 3H), 2.67 (m, 1H), 3.75 (s, 3H), 5.7–6.22 (m, 1H), 6.85 (d, 2H, 9), 7.19 (d, 2H, 9); ^{13}C-NMR δ (**5** and **6**) 20.27, 20.66, 32.96, 33.73, 34.94, 35.05, 35.20, 43.57, 47.08, 54.06, 55.02 (2C), 113.12, 113.76 (4C), 126.71, 126.87, 127.52 (2C), 128.44 (2C), 135.84, 138.10, 141.78, 157.92, 158.10; calc for $C_{13}H_{18}O$: 202.135757; meas: 202.136310.

Synthesis of 1,5-*dimethyl*-4-(4′-*methoxyphenyl*)*cyclohexene* (**10**)

The general procedure was followed except for a 9.85:1 isoprene/**1** ratio and an 8 min reaction time. Thick layer chromatography afforded 60.3 mg (0.28 mmol, 21.8%) of a clear, pale yellow oil: GCMS revealed only one product peak: 216 (M^+), 148 (100); ^{1}H-NMR δ 0.7 (d, 3H, 6), 1.26 (m, 1H), 1.66 (s, 3H), 1.91–2.5 (m, 5H), 3.76 (s, 3H), 5.46 (bs, 1H), 6.84 (d, 2H, 9), 8.2 (d, 2H, 9); ^{13}C-NMR δ 20.25, 23.36, 34.02, 35.29, 39.92, 47.02, 55.19, 113.76 (2C), 120.94, 128.51 (2C), 133.77, 138.22, 157.85; calc for $C_{15}H_{20}O$: 216.151406; meas: 216.151707.

Synthesis of 4-(4′-*methoxyphenyl*)-3,5,6-*trimethylcyclohexenes*: (±)-4*S*,3*S*,5*S*,6*R*-(**19**) *and* (±)-4*S*,3*R*,5*S*,6*S*-(**20**)

A 2.86 *E*,*E*-2,4-hexadiene (**18**)/**1** ratio was employed with the usual procedure affording upon distillation (115–140°, 1 Torr) 303.9 mg (1.32 mmol, 42%) of a 1:1 (GC) mixture of isomers **19** and **20**; GCMS showed two peaks with identical spectra: 230 (M^+), 148 (100); ^{1}H-NMR (**19** and **20**) δ 0.5–1.23 (m, 9H), 1.23–2.5 (m, 3H), 2.71 (dd, 1H, 5 and 6), 3.7 (s, 3H), 5.62 (m, 2H), 6.83 (d, 2H, 9), 7.18 (d, 2H, 9); ^{13}C-NMR (**19** and **20**) δ 15.31, 16.89, 17.35, 18.31, 20.28, 20.69,

33.25, 35.31, 36.37, 36.73, 39.22, 39.51, 49.18, 50.56, 55.15 (2C), 113.30 (2C), 113.59 (2C), 129.18 (2C), 130.19 (2C), 131.78, 131.96, 132.43, 132.60, 135.66, 136.96, 157.70, 157.84; calc for $C_{16}H_{22}O$: 230.167055; meas: 230.166614.

Synthesis of (±)-*4S-(4'-methoxyphenyl)-1,2,5S-trimethylcyclohexene* (**22**)

A 2.95:1 ratio of **21/1** used with the usual procedure afforded after chromatography 173.3 mg (0.752 mmol, 55.2%) of liquid **22**: GCMS showed one peak: 230 (M^+), 148 (100); ^{1}H-NMR δ 0.7 (d, 3H, 6), 1.62 (s, 6H), 1.7–2.6 (m, 6H), 3.78 (s, 3H), 6.75 (d, 2H, 9), 7.12 (d, 2H, 9); ^{13}C-NMR δ 18.66 (2C), 20.02, 34.33, 41.71, 41.86, 47.90, 55.18, 113.78 (2C), 125.29, 125.47 (2C), 128.47, 138.24, 157.85; calc for $C_{16}H_{22}O$: 230.167055; meas: 230.166395.

Synthesis of (±)-*4S-(4'-methoxyphenyl)-1,3S,5S-trimethylcyclohexene* (**24**) *and* (±)-*4S-(4'-methoxyphenyl-1,3R,5S-trimethylcyclohexene* (**25**)

Isolated, after chromatography 123.6 mg (0.54 mmol, 42%) of a 5.4:1 mixture (GC) of **24/25** from the reaction of a 1.03 ratio of diene **23/1**: GCMS showed two product peaks with identical spectra: 230 (M^+), 148 (100); ^{1}H-NMR (**24**) δ 0.71 (d, 3H, 6), 0.85 (d, 3H, 6), 1.67 (d, 3H), 1.8–2.45 (m, 4H), 2.6 (dd, 1H, 5 and 6), 3.89 (s, 3H), 5.46 (bs, 1H), 6.84 (d, 2H, 9), 7.09 (d, 2H, 9); ^{13}C-NMR (**24**) δ 16.95, 20.57, 23.41, 26.86, 35.72, 39.73, 50.13, 50.44, 113.25, 127.75, 130.10, 132.09, 135.54, 157.66; calc for $C_{16}H_{22}O$: 230.167055; meas: 230.166395.

Synthesis of (±)-(**27**) *and* (±)-(**28**)

A 0.57 ratio of 1,1'-dicyclopentenyl/**1** was reacted in the usual manner to afford after column chromatography, removal of most of unreacted **1** (120°, 1 Torr), and thick layer chromatography, 142.4 mg of material which by GC consisted of 84.2% **27**+**28** and 15.8% **1**. Thus, 117.34 mg (0.42 mmol, 16%) of **27**+**28** were actually obtained: GCMS showed two product peaks in a 4.88 ratio (**27/28**) with identical mass spectra: 282 (M^+), 148 (100), ^{1}H-NMR (**27**) δ 0.85 (d, 3H, 6), 0.3–3.2 (m, 16H), 3.72 (s, 3H), 6.8 (d, 2H, 9), 7.92 (d, 2H, 9); ^{13}C-NMR (**27**) δ 18.43, 22.74, 24.83, 27.33, 29.46, 30.25, 33.46, 37.80, 46.38, 49.46, 50.36, 55.04, 113.33 (2C), 129.47 (2C), 134.19 (2C), 136.49, 157.63; calc for $C_{20}H_{26}O$: 282.198354; meas: 282.198988.

Synthesis of 2-(*4'-methoxyphenyl*)-1-*methyl*-3-(*2'-methylpropenyl*)*cyclobutane* (**30**)

In the usual procedure, a 2.006 ratio of **29/1** was reacted affording, after column chromatography and distillation, 236.2 mg (1.03 mmol, 34.4%) of a clear colorless oil: GCMS showed one peak: 188 (M^+-42), 148 (100); ^{1}H-NMR δ 1.1 (d, 3H, 6), 1.5 (s, 3H), 1.65 (s, 3H), 2.3 (m, 1H), 2.3 (m, 2H), 2.60 (t, 1H, 9), 2.9 (quintet, 1H, 9), 3.75 (s, 3H), 5.2 (d, 1H, 9), 6.8 (d, 2H, 9), 7.2 (d, 2H, 9); ^{13}C-NMR δ 18.25, 20.69, 25.64, 34.52, 35.39, 39.03, 55.13, 55.42, 113.67, 127.46, 129.53, 131.13, 136.42, 157.94; calc for $C_{16}H_{22}O$: 230.167055; meas: 230.167271.

Attempted reaction between **1** *and 2E,4Z-hexadiene* (**31**)

The ratio of **31/1** was 9.56 (**31**: 97% *E,Z* and 3% *E,E* by GCMS; Albany International). No DTBP and only 16.7 mol% of the aminium salt was employed. Column chromatography followed by distillation (115–140°, 1 Torr) afforded 525.9 mg (2.28 mmol, 39.22%) of a clear viscous oil which consisted of two isomeric products which were identical in all respects (^{1}H- and ^{13}C-NMR, GCMS) to adducts **19** and **20**.

Attempted reaction of **1** *with 2-methyl-2,4E-hexadiene* (**32**)

Following the usual procedure, a 2.87 **32/1** ratio afforded mainly the dimer of **1** and a trace of a probable cycloadduct: GCMS showed one adduct peak: 244 (M^+), 148 (100); the fragmentation pattern was typical of known cycloadducts.

Synthesis of 4-(*4'-methoxyphenyl*)-1,3,3,5-*tetramethylcyclohexene* (**34**) *and* 2-(*4'-methoxyphenyl*)-1,3-*dimethyl*-1-(*2'-methylpropenyl*)*cyclobutane* (**35**)

With the usual method, a 1.52 **33** (2,4-dimethyl-1,3-pentadiene): **1** ratio afforded a 7/2 (by ^{1}H-NMR; olefinic region) mixture of isomeric products which was isolated via thick layer chromatography as a clear viscous oil: GCMS showed only one product peak: 244 (M^+), 148 (100); ^{1}H-NMR (**34**) δ 0.7 (d, 3H, 5), 0.72 (s, 3H), 0.78 (s, 3H), 1.62 (s, 3H), 1.70–2.30 (m, 4H), 3.85 (s, 3H), 5.21 (s, 1H), 6.82 (d, 2H, 9), 7.09 (d, 2H, 9); (**35**: clearly assignable signals) δ 1.09 (d, 3H, 6), 1.52 (s, 3H), 1.62 (s, 3H), 5.45 (s, 1H); ^{13}C-NMR (**34**) δ 20.81, 23.35, 24.78, 26.14, 28.87, 30.05, 40.65, 55.15, 57.62, 112.90, 113.61, 130.33, 133.45, 135.27, 157.97; calc for $C_{17}H_{24}O$: 244.182704; meas: 244.183241.

Synthesis of 1-(*4'-methoxyphenyl*)-3-*methyl*-2-(*2'-methylpropenyl*)*cyclobutane*

Following the usual procedure, a 2.80 diene (**32**)/4-vinylanisole ratio afforded, after thick layer chromatography and distillation, 58.3 mg (0.253 mmol, 28%) of a clear colorless oil: GCMS showed one significant product peak: 230 (M^+), 134 (100), ^{1}H-NMR δ 1.09 (d, 3H, 6), 1.41–3.15 (m, 5H), 1.66 (s, 3H), 1.71 (s, 3H), 3.76 (s, 3H), 5.22 (d, 1H, 9), 6.72 (d, 2H, 9), 7.12 (d, 2H, 9); ^{13}C-NMR δ 18.43, 20.41, 25.79, 34.34, 34.95, 43.57, 50.98, 55.21, 113.61, 127.34, 128.73, 131.78, 137.52, 157.79; calc for $C_{16}H_{22}O$: 230.167055; meas: 230.166614.

Acknowledgement—The authors thank the National Science Foundation (CHE-8121700) and the Welch Foundation (F-140) for support of this research.

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