extracted with ether (×3), dried over Na_2SO_4, and fractionally distilled to yield 5.0 g of low-purity (76% by GC analysis) 1-bromo-1-methylcyclopropane (bp 78–80 °C (lit.[63] bp 72–85 °C)). Further purification by preparative GC gave 1.89 g (20.9% yield) of material with 99.98% purity. ^{1}H NMR: Me_2SO, $(CH_3)_4Si$ (int), δ 0.75–1.1 (m, 4 H, ring *H*), 1.7 (s, 3 H, C–C*H*$_3$). MS: *m/e* (relative intensity) 55 (100), 134 (3.22, M^+, ^{79}Br), 136 (3.10, M^+, ^{81}Br).

1-Bromo-1-ethoxycyclopropane. Ethyl 3-chloropropionate (6.83 g, 50 mmol) and sodium (2.3 g, 100 mmol) in diethyl ether (Bouveault–Blanc condensation) in the presence of trimethylchlorosilane (5.43 g, 50 mmol) gave on distillation 1-ethoxy-1-(trimethylsilyloxy)cyclopropane[64] (1.15 g, 6.6 mmol, 13.2% yield). The last named compound was reacted with PBr_3 as described by Gadwood[65] to give 1-bromo-1-ethoxycyclopropane. Preparative GC of this compound gave 0.55 g (6.7% yield based on ethyl 3-chloropropionate) of material with 90.2% purity. ^{1}H NMR: $CDCl_3$, $(CH_3)_4Si$ (int), δ 1.15 (m, 7 H, ring *H* and CH_2CH_3), 3.60 (q, 2 H, OCH_2CH_3, J = 7 Hz) in agreement with the literature.[65] MS: *m/e* (relative intensity) 57 (100), 164 (15.7, M^+, ^{79}Br), 166 (15.5, M^+, ^{81}Br).

1-Bromo-1-methoxycyclopropane. This compound was prepared from methyl 3-bromopropionate following the procedure outlined above for the ethoxy derivative.[64,65] Preparative GC gave 1-bromomethoxycyclopropane (0.5 g, 10% yield based on starting methyl 3-bromopropionate) with 97.0% purity. ^{1}H NMR: $CDCl_3$, $(CH_3)_4Si$ (int), δ 1.3 (s, 4 H, ring *H*), 3.4 (s, 3 H, OCH_3). MS: *m/e* (relative intensity) 41 (100), 150 (13.6, M^+, ^{79}Br), 152 (13.6, M^+, ^{81}Br).

(1-^{13}C)-1-Bromo-1-ethoxycyclopropane. Reaction of $Na^{13}CN$ with ethylenechlorohydrin by a literature procedure[66] gave ethylenecyanohydrin-^{13}*C* which was then hydrolyzed with concentrated HCl[67] to form (1-^{13}C)-3-chloropropionic acid. This acid was esterified in refluxing ethanol with *p*-toluenesulfonic acid as catalyst. The resultant (1-^{13}C)-3-chloropropionate was converted[64,65] as described above to (1-^{13}C)-1-bromo-1-ethoxycyclopropane. Preparative GC gave a product (0.1 g, 6.6% yield based on ethylenechlorohydrin) with 89.5% purity. ^{1}H NMR: $CDCl_3$, $(CH_3)_4Si$ (int), δ 1.1 (m, 7 H, ring *H* and CH_2CH_3), 3.6 (m, 2 H, $^{13}COCH_2CH_3$). MS: *m/e* (relative intensity) 58 (100), 165 (12.0), 167 (11.2).

1-Bromo-1-chlorocyclopropane. Cyclopropanecarboxylic acid chloride (57 g, 548 mmol) was treated at 135 °C (oil bath) for 1.5 h with *N*-chlorosuccinimide (144 g, 1082 mmol). 1-Chlorocyclopropane-1-carboxylic acid chloride was formed in 14% yield (7.9 g, GC analysis). Since trial experiments had shown that reaction for a longer time gave only over-chlorinated products, the crude reaction mixture was fractionally distilled (32–34 °C (10 mmHg)) to obtain 53.5 g of a mixture containing 10% (GC analysis) 1-chlorocyclopropane-1-carboxylic acid chloride and 90% cyclopropanecarboxylic acid chloride. This mixture was cooled to 0 °C and then treated dropwise with cooled (0 °C) acetone (136 mL). This was followed by the dropwise addition of a solution containing 98 g (1166 mmol) of $NaHCO_3$ in 700 mL of water, the internal temperature of the reactants being maintained at <7 °C. The solutiuon was cooled to 0 °C, and concentrated HCl (90 mL) was added dropwise (internal temperature <5 °C). Extraction with CH_2Cl_2 (3 × 300 mL), drying over Na_2SO_4, and removal of solvent at 25 °C gave 38 g of a colorless liquid containing (GC analysis) 10% 1-chlorocyclopropanecarboxylic acid and 90% cyclopropanecarboxylic acid. Fractional distillation gave 3.6 g of 76% pure 1-chlorocyclopropane-1-carboxylic acid: bp 102–104 °C (10 mm Hg), mp 70–72 °C (lit.[68] bp 206 °C (760 mmHg), mp 70–71 °C); yield 6.3% (based on cyclopropanecarboxylic acid chloride). MS: *m/e* (relative intensity) 85 (100), 120 (72.5, M^+, ^{35}Cl), 122 (23.7 M^+, ^{37}Cl). This material (3.6 g, 30 mmol) was dissolved in $CHBr_3$ (36 mL) and treated with HgO (6.4 g, 30 mmol) with stirring at room temperature for 1 min and cooled to 0 °C, and Br_2 (6.1 g, 38 mmol) was added dropwise maintaining the internal temperature <12 °C. The yellow reaction mixture was then allowed to warm to room temperature, and stirring was continued for a further 16 h. The now colorless reaction mixture was suction filtered, and the filtrate was fractionally distilled to give 1-bromo-1-chlorocyclopropane (1.8 g, 76% purity, bp 25 °C (50 mmHg)). Preparative GC gave 0.58 g (0.68% yield based on cyclopropanecarboxylic acid) of this compound with 99.3% purity. ^{1}H NMR: $CDCl_3$, $(CH_3)_4Si$ (int), δ 1.44 (s, 4 H, ring *H*). MS: *m/e* (relative intensity) 75 (100), 154 (6.9, M^+, ^{35}Cl, ^{79}Br), 156 (9.5, $(M + 2)^+$).

Registry No. 1-Bromo-1-methylcyclopropane, 50915-27-0; 1-bromo-1-ethoxycyclopropane, 95631-62-2; 1-bromo-1-methoxycyclopropane, 72282-90-7; 1-bromo-1-chlorocyclopropane, 108817-33-0; (1-^{13}C)-1-bromo-1-ethoxycyclopropane, 108817-34-1; methylenecyclopropane, 6142-73-0; ethyl 3-chloropropionate, 623-71-2; chlorotrimethylsilane, 75-77-4; 1-ethoxy-1-(trimethylsiloxy)cyclopropane, 27374-25-0; methyl 3-bromopropionate, 3395-91-3; cyclopropanecarbonyl chloride, 4023-34-1; 1-chlorocyclopropanecarbonyl chloride, 73492-25-8; 1-chlorocyclopropanecarboxylic acid, 108817-35-2; 1-methylcyclopropyl radical, 65338-31-0; 1-methoxycyclopropyl radical, 108817-36-3; 1-ethoxycyclopropyl radical, 108834-54-4; 1-chlorocyclopropyl radical, 33272-69-4; 1-methylcyclopropane, 594-11-6; 1-ethoxycyclopropane, 5614-38-0; cyclopropyltrimethylsilane, 930-40-5.

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(67) *Organic Syntheses*; Wiley: New York; Collect. Vol. I, pp 131–132.
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Mechanistic Diagnosis of Aminium Salt Initiated Diels–Alder Cycloadditions in the Diene/Diene Format

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Abstract: The aminium salt catalyzed Diels–Alder reaction has been subjected to mechanistic scrutiny. Eight discrete reaction systems in the diene/diene Diels–Alder format, including both dimerizations and cross additions, and also one cyclobutanation reaction, have been examined on the basis of as many as five distinct mechanistic criteria. The previously proposed cation radical chain mechanism is specifically confirmed and, among others, a Brønsted acid catalyzed mechanism ruled out in every instance except one. As previously proposed by another laboratory, the cyclodimerization of 2,4-dimethyl-1,3-pentadiene is found to proceed via a Brønsted acid catalyzed mechanism. These results support and further broaden similar conclusions based upon detailed kinetic studies on two cycloaddition systems, previously reported by this laboratory. Experimental procedures for performing these reactions and isolating and characterizing the cycloadducts are also reported.

Aminium salt initiation has been found to represent a powerful and highly stereoselective protocol for Diels–Alder[1-3] and other[4,5] cycloadditions and cyclodimerizations of ionizable substrates. The cation radical chain mechanism invoked for these reactions

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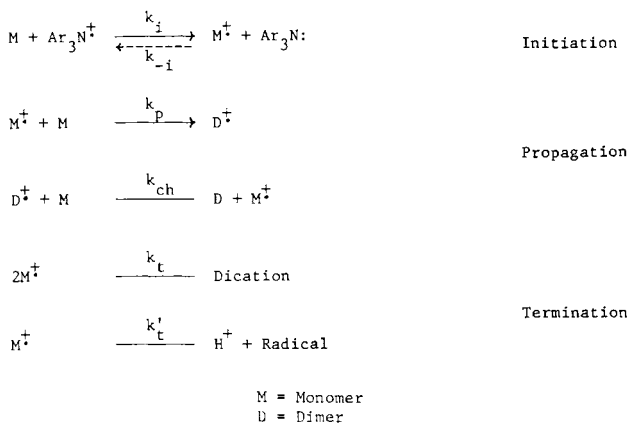
Scheme I

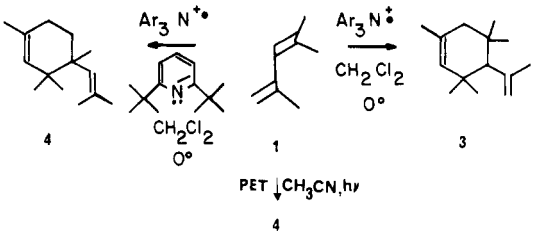


(Scheme I) was modeled directly upon Ledwith's classic mechanism[6] for the cyclodimerization of *N*-vinylcarbazole initiated by single-electron acceptors. Subsequently, one of the numerous cycloadditions reported by this laboratory has been found to occur, instead, via a Brønsted acid catalyzed mechanism, albeit one of the other cycloadditions reported by this laboratory was confirmed as proceeding via a cation radical chain mechanism.[7] These results naturally engendered an intensive review of the validity of the proposed cation radical chain mechanism in the remainder of the cycloadditions already reported. Moreover, a determination was made (and has been implemented) to subject all cycloadditions studied subsequently, whether carried out by the aminium salt or other cation radical protocol, to individual mechanistic screening. The present report deals specifically only with those cycloadditions which had already been published prior to the report[7] of the potential of the aminium salt for effecting Brønsted acid catalyzed cycloaddition. Screening of reactions observed subsequently is a standard aspect of the characterization and is included in the subsequent papers in which the new cycloadditions are reported. It should suffice to state that *no* further examples of Brønsted acid catalysis under aminium salt conditions have emerged in the numerous (certainly >75) cycloadditions observed since the time of the report of Brønsted acid catalysis.

Aminium salt initiated cation radical Diels–Alder cycloadditions require an ionizable component, usually a conjugated diene, styrene, or electron-rich alkene.[8,9] Correspondingly, three discrete formats for cation radical Diels–Alder reactions have been recognized: diene/diene, diene/styrene, and diene/electron-rich alkene. The particular aminium salt reaction which has emerged as Brønsted acid catalyzed is of the diene/diene format. This class of cycloadditions is therefore afforded special emphasis in this study.

The Brønsted Acid Catalyzed Mechanism. The facile Diels–Alder cyclodimerization of 2,4-dimethyl-1,3-pentadiene (**1**, Scheme II) in the presence of tris(4-bromophenyl)aminium hexachloroantimonate (**2**$^{\bullet+}$) was one of several diene cyclodimerizations reported from this laboratory and considered to exemplify the cation radical Diels–Alder reaction.[2] Evidence that the observed cyclodimerization of **1** under aminium salt conditions actually occurs via a Brønsted acid catalyzed path is now overwhelming.[7] Not only does an authentic Brønsted acid catalyzed reaction afford the same cyclodimer (**3**) in an equally facile manner, but a different cyclodimer (**4**, Scheme II) is produced in the photosensitized electron-transfer cyclodimerization of **1**, which is considered to represent an authentic cation radical Diels–Alder cyclodimerization. Perhaps most convincingly of all, the presence of 2,6-di-*tert*-butylpyridine in a molar amount exceeding that of the aminium salt catalyst completely inhibits the reaction leading to dimer **3** and, instead, in a somewhat slower reaction, cyclodimer **4** is generated.[7,10] Analogous investigations of the cyclodimerization of 1,3-cyclohexadiene, as mentioned previously, tend to confirm the cation radical chain mechanism.[7] The present paper reports results of the application of these and additional mechanistic tests to the remaining aminium salt initiated diene/diene cycloadditions as described above. In addition to the diagnostic testing, experimental procedures for carrying out these cycloadditions[1,2] and for the characterization of the cycloadducts are reported.

Scheme II. Cyclodimerization Modes of 2,4-Dimethyl-1,3-pentadiene: The "PET" and Hindered Base Criteria



Mechanistic Criteria

The necessity for mechanistic distinction between cation radical chain and Brønsted acid catalyzed reactions has recently become apparent.[7] Several criteria have been reported in brief form, and a few others have been explored in the present work. Consequently, a brief description and commentary on each of the criteria utilized in this study appears of general interest.

The 2,6-Di-*tert*-butylpyridine (Hindered Base, 5) Criterion. The sterically highly hindered nature of **5** restricts its nucleophilic reactivity to protons. Consequently, it is plausible to hypothesize that, while a Brønsted acid catalyzed reaction would be completely inhibited by a sufficient quantity of **5**, cation radical chains might continue to be propagated without interference. In the cycloaddition mechanism under consideration (Scheme I), the two chain carrying cation radicals are diene (M$^{\bullet+}$) and adduct (D$^{\bullet+}$) cation radicals, respectively. To the extent that such species prefer to react with unhindered pyridine bases as carbon electrophiles, reaction with **5** would clearly not be expected. Equally importantly, electron transfer from **5** to a chain-carrying cation radical would not be expected, either, since the lone pair of pyridine is relatively difficultly ionized ($E_{1/2}$ = 1.82 vs. SCE[11]). However, it should be recalled that many cation radicals, especially those with β protons, are quite strong acids and therefore potentially easily capable of reacting with **5** as proton donors.[12] This would be especially likely in a case where the cycloaddition is unusually slow. Consequently, a *caveat* concerning the use of the hindered base criterion is suggested, i.e., failure to inhibit is a reliable indication of the absence of a Brønsted acid catalyzed process, but inhibition, *especially if it is not complete*, is not a reliable positive indication for Brønsted acid catalysis. The acid that catalyzes the cyclodimerization is not presently known. It might be presumed to be $HSbCl_6$[7] but could even be one of the chain-carrying cation radicals. In any case, it is not merely traces of contaminating acid in the aminium salt that catalyze the dimerization of **1**, since inhibition is not complete until the molar amount of **5** exceeds that of **2**. Apparently, the generation of Brønsted acid is linked to the availability of **2**$^{\bullet+}$ and hence, in all

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(3) Bauld, N. L.; Bellville, D. J.; Pabon, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 5158.
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(6) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133.
(7) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 7993.
(8) Bauld, N. L.; Bellville, D. J., Pabon, R. A.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378.
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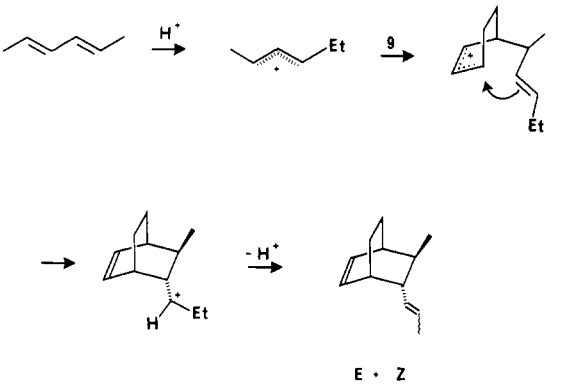
(12) Nicholas, A. M. de P.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165.

likelihood, to cation radical formation (e.g., $1^{\bullet+}$). It therefore remains conceivable that $1^{\bullet+}$ itself is the initiating Brønsted acid, though it is unlikely that this species is ever subsequently regenerated. Since termination of cation radical chain processes by proton loss has been observed,[13] it is also possible that $1^{\bullet+}$ merely serves as a source of $HSbCl_6$ through deprotonation. In either case the buildup of strong acid is required and is achieved via the agency of cation radicals. Since $1^{\bullet+}$ could be deprotonated by **5**, it is critical that the hindered base not only suppresses the formation of **3** but permits the formation of **4**.

The PET Cycloaddition Criterion. Photosensitized electron transfer appears to be a reliable method of generating cation radicals of a variety of ionizable substrates.[1,10,14,15] If cycloadditions, and indeed Diels–Alder cycloadditions, are an intrinsically preferred reaction mode of cation radicals, it should be possible to observe them with PET as an initiation procedure. This has indeed been documented in two other laboratories.[10,16] Further, since the aminium salt initiated cycloadditions previously reported were not only periselective but regioselective, the obtention of identical products in the two approaches has added significance. In some cases, periselectivity (Diels–Alder vs. cyclobutane selectivity) and/or diastereoselectivity (e.g., exo vs. endo selectivity) are incomplete and a fingerprint comparison becomes feasible. It is important to note that buildup of long-lived Brønsted acid under PET conditions (specifically, in acetonitrile with 1,4-dicyanobenzene as sensitizer) becomes much less likely, since the counterion of any cation radical or proton generated is a relatively basic anion radical capable of effectively quenching the former.[10] The *caveat* appropriate to the PET criterion is that the nonexistence or inefficiency of a particular PET-initiated cycloaddition is not necessarily informative with respect to whether the cycloaddition in question occurs under aminium salt conditions. This is a consequence of the fact that under PET conditions cation radicals may react with their gegenanion radicals extremely rapidly, by back-electron transfer, addition, or other means at a rate that could greatly exceed the rate of the Diels–Alder cycloaddition. Again, this scenario is especially likely when cycloaddition is unusually slow. Verification that an observed PET-initiated cycloaddition is indeed a cation radical cycloaddition, as opposed to direct photochemistry, is also essential. This is best handled by running parallel blank reactions omitting the sensitizer. Even under these circumstances, caution is recommended, since in a few instances back-electron transfer leads to triplets, which ultimately can yield cycloaddition products.[17] In the present context, such triplet reactions are easily distinguished in that they are normally characterized by modest cyclobutane periselectivity.[17]

Brønsted Acid Criterion. If a particular cycloaddition is Brønsted acid catalyzed, it should be possible to omit the aminium salt and provide a selected Brønsted acid of appropriate strength to catalyze the reaction. In previous research involving **1**, both HBr and $HSbCl_6$ ($HCl + SbCl_5$) proved adequate.[7] For greater convenience, the Brønsted acid selected for use in this work was triflic acid, an extremely strong organic acid. Dichloromethane was retained as the solvent, and the temperature (0 °C) and reactant concentrations were typical of the aminium salt initiated reactions. All reactions were carried out with use of a range of triflic acid concentrations (1–10 mol % relative to the monomer) over which the cycloadducts observed in the aminium salt reaction were verifiably stable, while monitoring the decomposition of reactants by GC and GCMS. The dimerization of **1** to **3** is thus accomplished in excellent yield in less than 2 min reaction time, comparable to the time frame of the aminium salt reaction.

Scheme III. Hypothetical Brønsted Acid Catalyzed Cycloaddition of *t,t*-**10** to **9**: The Stereochemical Criterion



Kinetic Criterion. Results of detailed kinetic studies of two aminium salt initiated cyclodimerizations have recently been submitted to this journal.[13] Cation radical chain mechanisms for these cyclodimerizations are strongly supported by the observed kinetic rate laws. Moreover, the rates of both of these reactions are strongly retarded by added tris(4-bromophenyl)amine (**2**), as would be expected of a cation radical chain mechanism. The oxidation potential of **2** is considerably lower than that of most organic substrates, including the two substrates involved in the kinetic study referred to above; thus **2** is able to intercept the chain carrying cation radicals and engender reversal of the initiation step (Scheme I). That **2** is not a sufficiently strong base to neutralize even the strong acid produced under aminium salt ionizable substrate conditions and is thus unable to inhibit the Brønsted acid catalyzed reaction is anticipated and was verified in a kinetic study of the dimerization of **1**.[13] The rate of the aminium salt initiated cyclodimerization of **1** is unaffected by added **2**. Consequently, it appears that rate retardation by added neutral triarylamine is a reliable and specific criterion for the cation radical chain mechanism. Since the application of this criterion requires a kinetic study, it has not been applied to all reactions included in this study, but it has proved particularly valuable in one specific instance in which the other criteria lead to somewhat ambiguous results.

Stereochemical Criterion. The Brønsted acid catalyzed cycloaddition mechanism requires initial protonation of the dienophilic diene to produce an allylic cation. No doubt the extreme ease of protonation of **1** to yield the 1,1,3,3-tetramethylallyl carbocation accounts at least partly for the unusually facile Brønsted acid catalyzed reaction of **1**. The presumed mechanism for the *hypothetical* Brønsted acid catalyzed cross addition of *trans,trans*-2,4-hexadiene to 1,3-cyclohexadiene is depicted in Scheme III. It is especially noteworthy that this mechanism leads to predicted stereorandomization of the pendant propenyl group. In the initial paper in this series the cycloaddition of *trans,trans*-, *cis,trans*-, and *cis,cis*-2,4-hexadiene to 1,3-cyclohexadiene was reported to be stereospecific not only with respect to the double bond undergoing cycloaddition but also with respect to the pendant double bond of the cycloadduct.[1] This would appear to clearly rule out a Brønsted acid catalyzed mechanism for these reactions. In general, it is proposed that retention of the stereochemistry of the pendant double bond is a reliable counterindication of the Brønsted acid catalyzed mechanism. Whether suprafacially stereospecific addition to the dienophilic double bond is expected for such a mechanism is not absolutely certain, but it appears unlikely to be highly stereospecific. If this speculation is indeed correct, a second stereochemical criterion is also available to negate the Brønsted acid catalyzed mechanism.

Results

Cyclodimerization of 1,1′-Dicyclopentenyl (6). The aminium salt and PET initiated cyclodimerizations of **6** proceed in 50 and 71% yield, respectively, affording the same (endo:exo) pair of Diels–Alder cyclodimers (Scheme IV) in similar proportions (6.6:1 vs. 5.9:1, respectively).[1,5] Both procedures are highly periselective

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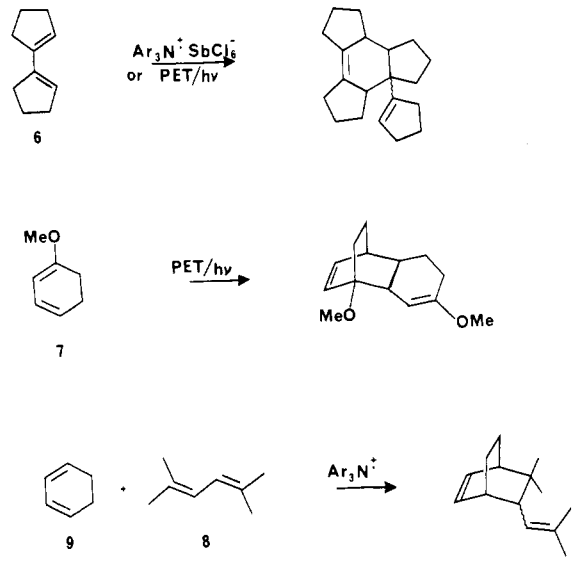
Scheme IV

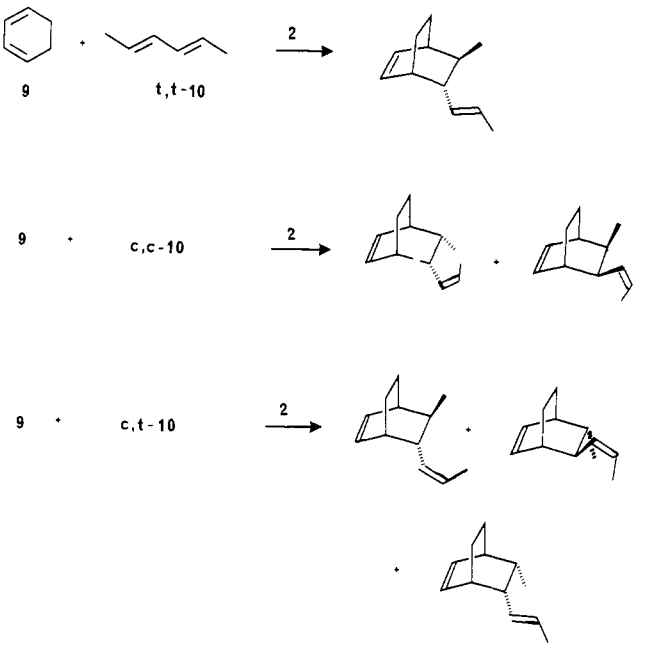


and produce no cyclobutanes or cyclooctadienes. For that matter, no other dimeric substances (linear or cyclic) are formed in as much as 1% yield. The PET-initiated reaction is also free of trimeric and other oligomeric adducts, which are formed to a minor extent in the aminium salt reaction. The hindered amine modified, aminium salt initiated reaction (92 mol % aminium salt/132 mol % 2,6-di-*tert*-butylpyridine) is actually more efficient than either of the former procedures, affording 85% of the same cyclodimer mixture. From a synthetic standpoint, the hindered base procedure is, however, grossly wasteful of the aminium salt. The fact that the procedure typically requires 50–100 mol % of the aminium salt to effect degrees of conversion which are readily achieved with only 3–5% of the aminium salt in the absence of the hindered amine is consistent with the proposal advanced previously that 2,6-di-*tert*-butylpyridine is capable of deprotonating chain-carrying cation radicals (e.g., $\mathbf{6}^{\bullet+}$) and thus decreasing chain length. However, it is also true that aminium salt is subject to decomposition by the hindered amine even in the absence of **6**. Finally, triflic acid catalyzed reaction of **6** revealed the formation of no less than *nine* discrete dimers in significant amounts. Although the two Diels–Alder cyclodimers formed in the aminium salt and PET initiated reactions are indeed present (50%), seven other dimers are formed, two of which, according to a relatively reliable mass spectral criterion (see Experimental Section), are also cyclodimers (25%), along with five more acyclic dimers (25% total). Both the aminium salt and PET cyclodimers are found to be stable under the reaction conditions (0 °C, CH_2Cl_2, 2.8 mol % triflic acid, 2.58 min), and the relative proportions of the nine dimers did not change significantly over the course of the triflic acid catalyzed reaction of **6**.

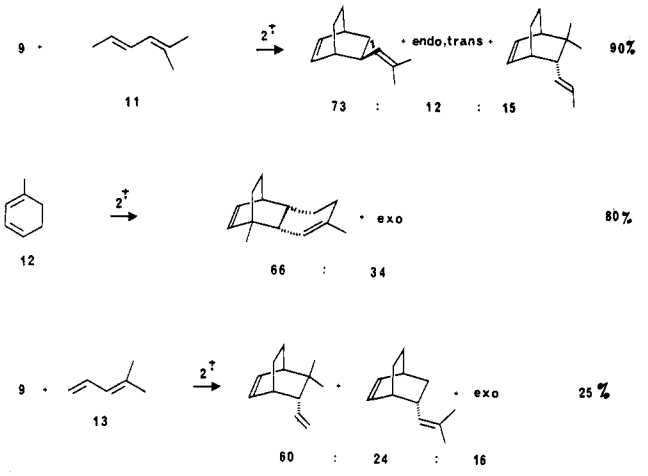
Cyclodimerization of 1-Methoxy-1,3-cyclohexadiene (7). The PET-initiated cyclodimerization of **7** is efficient (70%, Scheme IV).[3] The aminium salt initiated reaction produces the same cyclodimers (and no other cyclodimers), albeit in just trace amounts. However, inclusion of 2,6-di-*tert*-butylpyridine significantly increases the yield of these cyclodimers (17%). Independent tests on the latter cyclodimers reveal that their decomposition is effectively catalyzed by both Brønsted acids and $\mathbf{2}^{\bullet+}$. Presumably, inclusion of the hindered amine eliminates the Brønsted acid catalyzed decomposition mode, but consumption of the cyclodimers, which are enol ethers, by electron transfer to $\mathbf{2}^{\bullet+}$ continues to reduce the yield of these products. In view of the extreme susceptibility of the cyclodimers to acid catalyzed decomposition, the triflic acid catalyzed decomposition of **7** (which produces no cyclodimers) is rendered inconclusive.

Cycloaddition of 2,5-Dimethyl-2,4-hexadiene (8) to 1,3-Cyclohexadiene (9). The exceptional kinetic impetus of the cation radical Diels–Alder reaction was vividly illustrated, in the early work from this laboratory,[1] by the aminium salt initiated addition

Scheme V. Stereospecificity of the Diels–Alder Cycloaddition of **10** to **9**



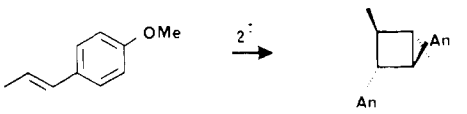
Scheme VI



of the hindered diene **8** to 1,3-cyclohexadiene (**9**, Scheme IV). The mechanistic profile of this reaction also turns out to be interesting and unusual. As reported by another laboratory, **8** completely quenches the normally facile PET-induced dimerization of **9** but fails to undergo cross addition with **9** or dimerization.[10] Effectively, though much electron-transfer chemistry undoubtedly transpires, the system is inert. The aminium salt initiated cross addition of **8** and **9** is retarded *but not completely* inhibited by 2,6-di-*tert*-butylpyridine. Triflic acid catalyzed treatment of 1:1 mixtures of **8** and **9** yielded no cross adducts at all, though linear dimers of both **8** and **9** were found. Since the mechanistic profile, at this point, appeared less definitive than that for any of the other reactions studied, the kinetic criterion was also applied. Addition of 100 mol % of **2** caused a retardation of the cycloaddition rate by a factor of 17. For comparison, the *trans*-anethole dimerization is retarded by a factor of 3.3 under very similar conditions by 100 mol % of **2**.

Other Cross Additions in the Diene/Diene Format. The addition of the three geometric isomers of 2,4-hexadiene (**10**) to 1,3-cyclohexadiene (**9**) was found to be stereospecific, not only with respect to the double bond undergoing addition but also with respect to the pendant propenyl group (stereochemical criterion, Scheme V). The PET-initiated reaction of *t,t*-**1** to **9** gave the same (single) cross adduct as the aminium salt reaction as well as the same two (exo and endo) cyclodimers of **9**.

Scheme VII



14

The addition of *trans*-2-methyl-2,4-hexadiene (**11**) to **9** also yielded the same three Diels–Alder cross adducts (Scheme VI) in both the aminium salt and PET initiated versions and in quite similar proportions. The same three cross adducts were also obtained in the hindered amine-modified aminium salt reaction. Triflic acid catalyzed decomposition of a 1:1 mixture of **11** and **9** gave none of these three cross cycloadducts, but a wide variety of other dimers and oligomers (especially trimers). The latter, according to the mass spectral criterion, were linear adducts. Similar results were obtained for the cyclodimerization of 1-methyl-1,3-cyclohexadiene (**12**) and the addition of 4-methyl-1,3-pentadiene (**13**) to **9** (Scheme VI).

Cyclodimerization of 1,3-Cyclohexadiene (9). The applications of the PET, hindered base, and Brønsted acid criteria have previously been reported by other laboratories.[7,10] The kinetic criterion has been applied in recent work, and a rate retardation of 2.2-fold by 25 mol % of **2** was observed.[13] The reaction is almost completely suppressed by 100 mol% of **2**.

Cyclodimerization of *trans*-Anethole (14). The PET-initiated reaction produces the same trans, anti, trans head-to-head cyclobutane cyclodimer as is obtained in the aminium salt reaction (Scheme VII), but in addition, competing direct photoisomerization of *trans*- to *cis*-anethole leads to an admixture of the various other geometric isomers of this cyclodimer.[4] In the presence of 2,6-di-*tert*-butylpyridine, the aminium salt initiated cyclodimerization of **14** occurs in significantly improved yield (75% vs. 45%). The triflic acid catalyzed decomposition of **12** produces none of the pertinent cyclodimer and indeed fails to yield any other detectable, volatile product. The addition of 100 mol % of **2** produces rate diminution by a factor of 3.3.

Discussion

Detailed kinetic studies reported in an earlier paper have already confirmed the Ledwith-type cation radical chain mechanism for the aminium salt initiated cyclodimerizations of 1,3-cyclohexadiene (**9**) and *trans*-anethole (**14**).[13] The present paper describes the application of five distinct mechanistic criteria to a variety of aminium salt initiated cycloadditions, including these two, now relatively well-studied, cases. The interpretation of the results detailed in the immediately previous section in light of the mechanistic criteria set forth earlier is quite straightforward. Only the cross cycloaddition of **8** and **9** appears to warrant special comment. A curious aspect of this reaction is that the PET version is ostensibly inert, i.e., not only does cycloaddition of **8** to **9** not occur, but even the normal PET-initiated cyclodimerization of **9** is completely quenched.[10] Undoubtedly $\mathbf{8}^{\bullet+}$ is formed, either in preference to or via $\mathbf{9}^{\bullet+}$, but its cycloaddition to **9** is apparently too slow to compete with chemistry which regenerates **8**, very probably back-electron transfer from the sensitizer anion radical. Steric effects provide a plausible basis for the unusually low rate of this cycloaddition. The hindered amine criterion also produces somewhat less than definitive results in its application to this reaction system.[7] The cycloaddition of **8** and **9** is indeed rather substantially retarded by excess 2,6-di-*tert*-butylpyridine but not, as would be expected for inhibition of a Brønsted acid catalyzed process and as is observed for the cyclodimerization of 2,4-dimethyl-1,3-pentadiene, completely so. The fact that authentic Brønsted acid catalyzed reaction between **8** and **9** does not produce any cross cycloadducts and, especially, that the rate is powerfully retarded by added **2** (kinetic criterion) nevertheless strongly suggests a cation radical mechanism for this reaction. The best explanation for the partial inhibition engendered by the hindered amine appears to be inhibition of the cation radical chain process by deprotonation of $\mathbf{8}^{\bullet+}$ or other chain-carrying cation radicals. The expected relatively low cycloaddition reactivity of $\mathbf{8}^{\bullet+}$ may render it especially susceptible to deprotonation.

Consequently, it now appears reasonable to conclude that the previously reported[7] cyclodimerization of 2,4-dimethyl-1,3-pentadiene (**1**) is the sole example of aminium salt initiated, Brønsted acid catalyzed cycloadditions encountered among the numerous aminium salt cycloadditions previously reported by us.[1,2] Moreover, the PET and kinetic criteria specifically identify the reactions as cation radical chain processes. The recognition of the possibility of Brønsted acid catalyzed Diels–alder cycloadditions under aminium salt conditions and the development of the hindered base and other criteria for distinguishing such processes from cation radical chain processes are, of course, extremely useful and has encouraged detailed mechanistic evaluation of all new reactions studied in this laboratory. Incidentally, at this point in time, no new examples of Brønsted acid catalyzed cycloadditions have emerged in the range of substrates encompassed in our investigations. It appears to the authors, therefore, that the scope of efficient, selective intermolecular Brønsted acid catalyzed Diels–Alder cyclodimerizations involving dienes in the dienophilic role is quite limited. The use of 2,6-di-*tert*-butylpyridine in a synthetic context, to increase yields, is not generally recommended, in view of the necessity for concomitant use of rather massive amounts of aminium salt initiator. Indeed, even the qualitative effect on yield is variable, as seen in the cross cycloaddition of **8** and **9**.

The present paper adds to the previous inventory of mechanistic criteria for distinguishing cation radical reactions (the PET, hindered base, and Brønsted acid criteria) two further criteria (kinetic and stereochemical criteria). Both are relatively more difficult to apply, but the kinetic criterion, in particular, promises to be a selective test for cation radical chain processes vis-à-vis not only Brønsted acid catalyzed processes but processes of any mechanistic classification.

Experimental Section

Analysis. Proton magnetic resonance (^{2}H NMR) spectra were recorded in deuterated chloroform on either a Varian EM-390 spectrometer for routine spectra at 90 MHz or a Nicolet NT-200 multinuclear spectrometer for 200-MHz FT spectra and proton-decoupling NMR studies. ^{1}H NMR chemical shifts are reported in δ, downfield from the internal tetramethylsilane standard. Carbon magnetic resonance (^{13}C NMR) spectra were determined in deuteriated chloroform on either a Varian FT-80A for routine spectra or a Bruker WH-90 FT spectrometer, utilizing a microsample technique and an external deuteriated water reference. Again, chemical shifts are reported in δ.

Low-resolution mass spectra (LRMS) were obtained on a DuPont 21-471 mass spectrometer. High-resolution mass spectra (HRMS) were obtained on a DuPont (CED) 21-110 mass spectrometer. Gas chromatography/mass spectra (GC/MS) were obtained on a Finnigan E1-C1 instrument utilizing an SE-30 coated 50 m capillary column and helium carrier gas. LRMS and GC/MS data processing was performed on an INCOS data system.

Analytical gas chromatography (GC) analyses were performed routinely on a Gow-Mac Series 550 gas chromatograph (thermal conductivity detection and helium carrier gas) utilizing a 4 ft × $^1/_8$ in. 5% OV-101 on Chromosorb P column. Preparative gas chromatography was performed on the Gow-Mac instrument utilizing a 10% SE-30 on Chromosorb W, 5 ft × 0.25 in. column unless otherwise noted. GC yields were calculated with the aid of a Hewlett Packard 3390A reporting integrator.

Infrared (IR) spectra were recorded on a Beckman AccuLab 7 infrared spectrometer with polystyrene film as a standard. Melting points were determined on a Mel-Temp capillary melting point apparatus. All melting points and boiling points reported herein are uncorrected.

Reagents. All solvents used, with the exception of practical grades used in some of the workups, were commercially available high-purity materials. Methylene chloride was distilled from phosphorus pentoxide and acetonitrile was distilled from calcium hydride prior to use. Both dry solvents were stored over molecular sieves.

All reagents commercially available were used as received unless otherwise noted. Glassware was oven dried where necessary. Anhydrous magnesium sulfate was used as the drying agent in all workups.

Generalized Triarylaminium Salt Procedure. Substrates to undergo the cation radical catalyzed Diels–Alder reaction or the olefin cyclodimerization reaction were mixed in dry methylene chloride in dilute quantities (0.1–0.5 M) in an oven-dried round-bottom flask. The solution was then cooled to 0 °C with stirring. Care need not be taken to exclude

oxygen, but excess adventitious water should not be present. Then a catalytic amount (5–10 mol %) of tris(*p*-bromophenyl)aminium hexachlorostibnate was added. These reactions were normally complete within 5–10 min, and product formation was monitored by GC analysis. Usually the blue color of the catalyst was decolorized, implying its consumption. The workup involved quenching any remaining cation radicals and cationic species present with methanol/methoxide solution and then pouring the mixture into a separatory funnel with the addition of excess methylene chloride. Then the crude organic solution was extracted three times with water to remove inorganic salts and once with saturated sodium chloride solution. The organic phase was then dried over anhydrous magnesium sulfate, filtered, and concentrated on the rotary evaporator. Purification was accomplished by preparative gas chromatography and, in some cases, by column chromatography on silica gel.

The yield of product(s) collected as a single peak via preparative GC was determined by first preparing a methylene chloride solution containing known amounts of the product and an internal standard. Biphenyl and naphthalene were suitable internal standards which are relatively inert to the reaction conditions. The thermal conductivity response factor relative to the standard was then determined. The corrected GC yield of the product(s) was obtained by repeating the reaction several times with a known amount of the internal standard present in the reaction mixture and averaging the results.

The products were characterized by GC/MS, HRMS, ^{1}H NMR, ^{13}C NMR, IR, and, where appropriate, proton decoupled ^{1}H NMR spectroscopy. Whenever possible, comparisons to literature spectra were made. The utilization of GC/MS was especially useful in product analysis. If a product was a Diels–Alder adduct, then the retro cation radical Diels–Alder in the mass spectrometer was apparent. The molecular ion peak in the mass spectrum was usually present but was relatively small, and the base peak in each case corresponded to the mass of the dienophilic component. Similarly, if the product was a cyclobutane adduct, then the retro cation radical [2 + 1] was observed. However, the molecular ion in these cases was exceptionally weak and sometimes even too small to observe, but these compounds still retained a base peak that corresponded to the most ionizable addend. Additionally, GC/MS was useful in determining the number and ratio of stereoisomers (*endo*/*exo* or *syn*/*anti*) appearing as a single peak when collected via preparative GC. In most cases, stereoisomers could not be separated. However, the capillary column used in the GC/MS analysis allowed base line resolution of stereoisomers in all cases, and isomer ratios were obtained by integration of the peaks.

Generalized Photosensitized Electron-Transfer Procedure. Unless otherwise noted, this procedure was followed routinely. A solution of the reactant(s) in dry acetonitrile containing 10–25 mol % of 1,4-dicyanobenzene (the electron-transfer sensitizer, Aldrich) was prepared in an oven-dried Pyrex test tube and capped. The tube was then hung in a water bath adjacent to a 450W Hanovia medium-pressure mercury-vapor lamp in a chilled water cooled quartz housing equipped with a Pyrex sleeve. The tube was irradiated at room temperature for at least 3 or 4 h before GC analysis. Usually sufficient product had been formed by then for isolation by preparative GC. However, a longer period of irradiation (up to 16 h or more) was required to achieve completion. In preparative runs, workup involved removal of the solvent by rotary evaporation, followed by extraction of the crude into hexanes or pentane, and then gravity filtration to remove 1,4-dicyanobenzene. Evaporation of the filtrate was followed by purification, which was usually accomplished by preparative GC and, in some cases, by column chromatography on silica gel. In each case, a parallel blank reaction (control) omitting only the electron-transfer sensitizer was irradiated to establish the neglibility of direct photoreactions bypassing the sensitizer.

The products were characterized with standard spectroscopic methods. GC/MS analysis was instrumental in determining the number and ratio of stereoisomers as well as confirming that the products were cycloadducts. The yields of products were obtained by irradiating to completion and then adding a known amount of biphenyl as an internal standard. By using the appropriate thermal conductivity response factor, corrected GC yields of the products were thus obtained.

General Procedure for Hindered Amine Studies. Because of decomposition of the aminium salt engendered by the hindered amine, it was found necessary to use relatively large amounts of the aminium salt, usually ca. 50 mol % relative to the addends.[18] In order to assure that any strong Brønsted acid which might be generated during the reaction is completely neutralized, an excess (usually ca. 60 mol %) of the hindered amine was typically employed.[7] The following procedure is illustrative: To a round-bottomed flask was added *trans*-anethole (197.7 mg, 1.33 mmol) and 2,6-di-*tert*-butylpyridine (142 mg, 0.74 mmol) in 5 mL of anhydrous dichloromethane. The solution was cooled to 0 °C and a solution of 478.8 mg (0.59 mmol) of tris(*p*-bromophenyl)aminium hexachloroantimonate in dichloromethane (5 mL) was then added as rapidly as possible via syringe. After 10 min the reaction was quenched with excess sodium methoxide/methanol and worked up with pentane and water. GC yields were obtained with biphenyl as an internal standard. GC/MS analysis revealed the formation of one major cyclodimer (the *trans,anti,trans*-cyclobutane head-to-head dimer) in 75% yield and no other significant dimeric products.

General Procedure for Triflic Acid Studies. As in the case of the hindered amine studies, addend concentrations were 0.13 M. For mixed additions, both addend concentrations were equal. Preliminary experiments established that little reaction of most addends occurred when 1 mol % of triflic acid was added; at 10 mol %, decomposition was too rapid. An optimum triflic acid level of 4.0 mol % was established and used as standard. Reactions again were carried out at 0 °C in dichloromethane. Reaction progress was monitored by GC. A typical procedure was as follows: 1,1′-Dicyclopentenyl (175.7 mg, 1.31 mmol) was dissolved in 5 mL of dichloromethane and cooled to 0 °C. Sufficient stock solution of triflic acid in dichloromethane was then added to deliver 3.7 mol % of the acid relative to the diene. The reaction was monitored by GC at 2, 7, 12, and 58 min. A 100-μL reaction aliquot was quenched with 50 μL of $KOCH_3/CH_3OH$. GC monitoring revealed that the ratios of the various products formed did not change during the reaction. GC/MS analysis (vide infra) revealed the presence of four cyclodimers and five linear dimers. Two of the cyclodimers were the ones formed in the conventional aminium salt initiated reaction. These cyclodimers were shown to be stable in the triflic acid solutions.

GC/MS Analysis. Product structures were inferred from GC/MS data on the basis of criteria developed in this laboratory during the last 5 years and found reliable without exception in a very large (>75) number of instances. In addition, the known products of the conventional aminium salt initiated or PET promoted cycloadditions were used in "spiking" experiments to confirm the structures of these cycloadducts in all cases. The criteria referred to above are the following: (1) Diels–Alder cycloadducts typically reveal a modest (10–20%) molecular ion ($M^{\cdot+}$) peak; however, the base peak corresponds to one of the two retro cation radical Diels–Alder fragments, both of which frequently appear as cation radical fragments. There is very little fragmentation in the region between the molecular ion and the retro Diels–Alder fragments. (2) Cyclobutane cycloadducts behave similarly in all respects except that the $M^{\cdot+}$ peak is either not observed at all or is extremely weak (ca. 1–5%) in normal EI spectra. (3) Cyclobutane adducts normally precede isomeric Diels–Alder adducts in order of elution on nonpolar GC columns. (4) Linear (noncyclic) adducts reveal a very strong molecular ion peak which is normally the base peak. In addition strong peaks corresponding to the loss of 1, 2, or more methyl (or ethyl) groups are invariably observed, and retro Diels–Alder fragmentation is virtually absent.

Kinetic Studies. The kinetic studies on 2,4-dimethyl-1,3-pentadiene and the 2,5-dimethyl-2,4-hexadiene/1,3-cyclohexadiene system were carried out on a Hewlett-Packard 8450A diode array spectrophotometer as in the previous study[13] but were only investigated at a single temperature (25 °C).

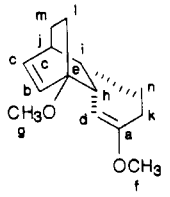
Tris(*p*-bromophenyl)amine. This amine was prepared according to a literature procedure.[18] To a solution of 23.9 g (97.4 mmol) of triphenylamine (Aldrich) in 150 mL of chloroform at 0 °C was slowly added a solution of 15 mL (290 mmol) of bromine (Baker Chemical Co.) in 40 mL of chloroform over 30 min. After being stirred for an additional 30 min, the product was obtained by the addition of 200 mL of hot absolute ethanol and then cooling to 0 °C and collecting by suction filtration. The precipitate was purified by Soxhlet extraction with methanol, yielding 37.7 g (80%; lit. 90%) of the product, mp 145–146.5 °C (lit. mp 144.5–146.5 °C).

Tris(*p*-bromophenyl)aminium Hexachlorostibnate. This cation radical salt was prepared according to a literature procedure.[19] To a solution of 6.24 g (13.3 mmol) of tris(*p*-bromophenyl)amine in 30 mL of dry methylene chloride at 0 °C was slowly added a solution of 2.9 mL (23 mmol) of antimony pentachloride (Aldrich). The reaction was instantaneous and the deep blue mixture which resulted was poured into 100 mL of cold, dry ether. The blue crystals were collected by suction filtration, washed thoroughly with dry ether, and vacuum dried at room temperature to yield 8.6 g (88% lit. 99%) of the product, mp 141–142.5 °C dec (lit. mp 141–142 °C). The cation radical salt is also available commercially (Aldrich); however, it was found desirable to thoroughly wash it with dry ether prior to use.

Photosensitized CRDA Dimerization of 1-Methoxy-1,3-cyclohexadiene (7). A solution of 7.7 g (70 mmol, actually 11.0 g of a 70% mixture commercially available from Aldrich) of 1-methoxy-1,3-cyclohexadiene (7) and 3.2 g (25 mmol, 25 mol %) of 1,4-dicyanobenzene (Aldrich) in 140 mL of dry acetonitrile was irradiated through a Pyrex filter for a

(19) Bell, F. A.; Ledwith, A.; Sherrington, D. C. *J. Chem. Soc. C* **1969**, 2719.

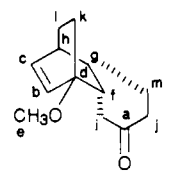
total of 32 h at room temperature by a 450W Hanovia medium-pressure mercury-vapor lamp housed in a water-cooled immersion jacket. The reaction was monitored by GC analysis of aliquots withdrawn periodically. Removal of the solvent by distillation, followed by removal of the unreacted minor isomer of **7** in vacuo afforded a semisolid residue. The residue was then treated with 20 mL of hexanes and gravity filtered to remove 1,4-dicyanobenzene. Removal of hexanes by distillation, followed by vacuum distillation (bp 122–125 °C (2.75 Torr)), yielded 3.8 g (50%) of dimer **15** as a light yellow oil. Purification of the dimer was also accomplished via preparative GC. The GC yield of the single peak corresponding to the dimer was determined to be 71% for a 1.0 M solution of **7** containing 28 mol % of the sensitizer after 16 h of irradiation. A control reaction omitting only 1,4-dicyanobenzene yielded no dimer. GC/MS indicated the single peak consisted of two major isomers in the ratio of 2:1. The mass spectrum of each isomer consisted of a parent peak at *m/e* 220 and a base peak at *m/e* 110. Exact mass calculated for $C_{14}H_{20}O_2$: 220.1463. Measured: 220.1465. Error: 0.2 mamu, 0.9 ppm. The ^{1}H NMR spectrum is consistent with Diels–Alder dimer **15** as an endo/exo pair (2:1). ^{1}H NMR ($DCDl_3$) [6.43 (d, exo) and 6.13 (d, endo), 2 H], [4.78 (d, endo) and 4.72 (d, exo), 1 H], [3.58 (s, exo) and 3.52 (s, endo), 3 H], [3.40 (s, endo and exo), 3 H], [2.8–1.1 (broad, endo and exo), 11 H]. The ^{13}C NMR spectrum was interpreted as follows



15

^{13}C NMR ($CDCl_3$) *endo*-**15**: (a) 156.7, (b) 133.6, (c) 130.8, (d) 91.6, (e) 79.1, (f) 52.7, (g) 49.2, (h) 40.5, (i) 35.8, (j) 34.1, (k) 27.6, (l) 26.6, (m) 25.7, (n) 22.6. ^{13}C NMR ($CDCl_3$) *exo*-**15**: (a) 156.7, (b) 133.6, (c) 130.8, (d) 90.2, (e) 78.7, (f) 53.0, (g) 49.6, (h) 38.9, (i) 36.6, (j) 33.6, (k) 27.2, (l) 25.7, (m) 25.3, (n) 21.0. The IR spectrum (thin film) contains an intense enol ether double bond stretch at 1662^{-1}.

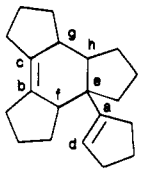
Hydrolysis of Dimer 15 to Ketone 16. To a solution of 1.013 g (4.598 mmol) of dimer **15** in 22 mL of methanol/water (4.5:1.0) at room temperature was added 0.0842 g (0.443 mmol, 9.6 mol %) of *p*-toluenesulfonic acid (Fisher Scientific Co.). After being stirred for 1.75 h, the solution was then extracted with four 20-mL portions of methylene chloride. The combined organic layers were dried and concentrated in vacuo to give 0.912 g (96%) of ketone **16** as a light yellow oil. GC/MS determined the ketone **16** to consist of two isomers in the ratio of 2:1. The mass spectra of both isomers consisted of a parent peak at *m/e* 206 and a base peak at *m/e* 110. Exact mass calculated for $C_{13}H_{18}O_2$: 206.1307. Measured: 206.1310. Error: 0.3 mamu, 1.5 ppm. The ^{1}H NMR spectrum was consistent with ketone **16** as an endo/exo pair (2:1). ^{1}H NMR ($CDCl_3$) [6.55 (m, exo) and 6.35 (m, endo), 2 H], [3.4 (two singlets barely resolved, endo and exo), 3 H], [2.8–1.3 (br, endo and exo), 1]. The ^{13}C NMR spectrum was interpreted as



16

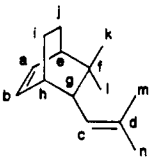
^{13}C NMR ($CDCl_3$) *endo*-**16**: (a) 211.2, (b) 133.2, (c) 131.8, (d) 78.4, (e) 49.0, (f) 38.5, (g) 37.3, (h) 35.5, (i) 34.5, (j) 33.7, (k) 25.9, (l) 25.7, (m) 23.0. ^{13}C NMR ($CDCl_3$) *exo*-**16**: (a) 211.5, (b) 133.8, (c) 131.8, (d) 77.6, (e) 49.5, (f) 38.3, (g) 37.6, (h) 36.5, (i) 34.5, (j) 33.1, (k) 25.9, (l) 25.1, (m) 19.1. The IR spectrum (thin film) contains a carbonyl stretch at 1712 cm^{-1}.

Photosensitized CRDA Dimerization of 1,1′-Dicyclopentenyl (6). A solution of 0.285 g (2.12 mmol) of 1,1′-dicyclopentenyl (**6**) in 2 mL of dry acetonitrile containing 0.065 g (0.51 mmol) or 24 mol % 1,4-dicyanobenzene was irradiated for 16 h. The product precipitated out of solution as a yellow oil so 1 mL of methylene chloride was added to ensure homogeneity for GC analysis. Two peaks were observed by GC in a total yield of 71% in what appears to be a cleaner reaction than the triarylaminium salt reaction of **6** since no trimers are observed. The two peaks were isolated individually by preparative GC. No product was observed in the control reaction. GC/MS analysis of the solution determined the two peaks to be isomers in a ratio of 5.85:1.00. The mass spectrum of each isomer consisted of a parent peak at *m/e* 268 and a base peak at *m/e* 134. Exact mass calculated for $C_{20}H_{28}$: 268.2191. Measured: 268.2186. Error: 0.5 mamu, 1.9 ppm. The ^{1}H NMR and ^{13}C NMR spectra are consistent with an endo/exo pair (5.85:1.00) of Diels–Alder dimers. ^{1}H NMR ($CDCl_3$) of the endo dimer: 5.30 (m, 1 H, olefinic), 2.5–1.0 (br, 27 H, allylic and aliphatic). ^{1}H NMR ($CDCl_3$) of the exo dimer: 5.35 (m, 1 H, olefinic), 2.5–0.07 (br, 27 H, allylic and aliphatic). The ^{13}C NMR spectra are interpreted as follows



^{13}C NMR ($CDCl_3$) of the endo dimer: (a) 150.8, (b) 133.8, (c) 133.2, (d) 122.3, (e) 52.9, (f) 51.4, (g) 50.3, (h) 47.5, the rest are unassigned (12 carbons)—38.2, 33.9, 33.7, 33.2, 31.1, 28.9, 28.7, 28.3, 25.4 (2 carbons), 24.4, 23.4. ^{13}C NMR ($CDCl_3$) of the exo dimer: (a) 152.2, (b) 133.4, (c) 133.1, (d) 119.4, (e) 52.0, (f) 48.0, (g) 46.7, (h) 43.1, the rest are unassigned (12 carbons)—34.5, 31.8, 31.2, 30.5, 29.5 (w carbons), 28.8, 27.8, 26.1, 25.8, 24.3, 23.1. IR (CH_2Cl_2) 2860, 2905, 1695, 1425, 1255, 1030 cm^{-1}.

CRDA Reaction of 9 and 2,5-Dimethyl-2,4-hexadiene (8). Fifty milliliters of a dry methylene chloride solution containing 0.654 g (8.16 mmol) of **9** and 0.479 g (4.35 mmol) of 2,5-dimethyl-2,4-hexadiene (**8**) (Aldrich) was stirred at ice bath temperature (0 °C). Then 0.472 g (0.578 mmol) or 13.3 mol % (based on **8**) of the aminium salt was added. Two separable peaks were observed to form by GC. The GC yield of the first peak, the Diels–Alder adducts **17**, was 61.3% (based on starting **8**). The remaining product peak was that corresponding to the Diels–Alder dimer of **9**, formed in 21.8% GC yield. GC/MS confirmed that the GC peak corresponding to the adducts **17** was indeed composed of only two major components (4:3). The parent mass was not present in either mass spectrum, and the base peak was *m/e* 110, corresponding to the mass of **8**. The HRMS of this mixture did locate the parent mass at *m/e* 190.1724, Calcd 190.1722. The ^{1}H NMR is consistent with a 4:3 mixture of *endo*-**17** and *exo*-**17**: ^{1}H NMR ($DCCl_3$) [6.4–6.0 (m, endo and exo), 2 H (bicyclic olefin)], [5.25 (d, exo) and 4.8 (d, endo), 1 H (exocyclic olefin)], [2.3–1.0 (br, endo and exo), 7 H], [1.65 (s, exo), 160 (s, exo), 1.55 (s, endo), 6 H (methyls attached to double bonds)], [1.60 (s, exo; methyl, exo face), 0.78 (s, endo; methyl, endo face), 0.78 (s, endo; methyl, exo face), and 0.6 (s, exo; methyl, endo face, 6 H (methyls attached to saturated sites)]. The ^{13}C NMR of this mixture was interpreted as follows

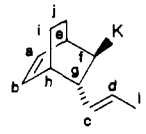


17

^{13}C NMR ($DCCl_3$) *endo*-**17**: (a) 133.8 (133.9), (b) 136.7 (133.9), (c) 130.9 (128.6), (d) 125.3 (127.5), (e) 38.2 (40.7), (f) 43.2 (44.9), (g) 49.9 (54.1), (h) 37.4 (31.0), (i) 27.3 (26.8), (j) 25.3 (26.4), (k) 33.4 (29.6), (l) 31.1 (29.6), (m) 17.1 (21.3), (n) 21.3 (26.3). ^{13}C NMR ($DCCl_3$) *exo*-**17**: (a) 134.8 (133.9), (b) 136.7 (134.3), (c) 129.1 (128.6), (d) 129.0 (127.5), (e) 39.1 (40.7), (f) 43.0 (44.9), (g) 45.6 (54.1), (h) 35.0 (31.0), (i) 26.2 (26.4), (k) 33.4 (30.0), (l) 31.1 (29.2), (m) 17.9 (21.3), (n) 22.1 (26.3). The numbers in parentheses are calculated chemical shifts.

CRDA Reaction of 9 and *trans*,*trans*-2,4-Hexadiene (10). A mixture of 0.597 g (7.45 mmol) of **9**, 0.545 g (6.64 mmol) of *trans*,*trans*-2,4-hexadiene (**10**) (Albany International), and about 50 mL of dry methylene chloride was stirred at 0 °C. To this solution was added 0.320 g (0.392 mmol) or 5.9 mol % (based on *t*,*t*-**10**) of the aminium salt. The reaction was followed by GC and two resolvable product peaks were observed to form. The GC yield of the first peak, the Diels–Alder adduct **18**, was determined to be 21.4% (isolated 18.9%), based on *t*,*t*-**30**. The second peak corresponded to the Diels–Alder dimers of **9** in 30.3% GC yield. GC/MS on the first product peak revealed two isomers to be present in a ratio of 65.7:1.0. Both of these compounds had mass spectra that possessed a parent peak at *m/e* 162 and a base peak at *m/e* 82. The HRMS parent mass was determined to be 162.1413, calcd 162.1409. ^{1}H NMR ($DCCl_3$): 6.2 (m, 2 H, bicyclic olefin), 5.5–4.9 (m, 2 H, exocyclic olefin), 2.2 (m, 3 H, allylic methines), 1.8–0.7 (br, 5 H), 1.6 (d, 3 H,

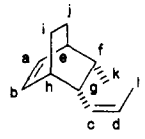
methyl attached to exocyclic double bond), 0.9 (d, 3 H, methyl attached to a saturated site on the exo face). The ^{13}C NMR was interpreted as follows



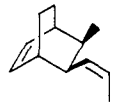
18

^{13}C NMR ($DCCl_3$) *endo*-**18**: (a) 131.2 (134.3), (b) 136.2 (134.3), (c) 137.1 (136.5), (d) 121.9 (121.5), (e) 36.3 (31.0), (f) 38.9 (40.3), (g) 50.6 (51.6), (h) 35.7 (31.0), (i) 26.4 (29.0), (j) 18.9 (28.6), (k) 17.6 (22.1), (l) 17.4 (18.8). IR (neat) 3020, 3010, 1735, 970, and 705 cm^{-1}.

CRDA Reaction of 9 and *cis,cis*-2,4-Hexadiene (10). A mixture of 0.470 g (5.85 mmol) of **9**, 0.515 g (6.28 mmol) of *cis,cis*-2,4-hexadiene (**10**) (Chemical Samples Co.), and 50 mL of dry methylene chloride was cooled to 0 °C before 0.414 g (0.507 mmol) or 8.07 mol % of the aminium salt was added. The reaction was followed by GC and two resolvable product peaks were observed to form, the latter of which was the Diels–Alder dimer of **9** in 30.8% GC yield, based on starting **9**. The first peak was determined to be the Diels–Alder adducts **19** and **20** in a total GC yield of 20.4% (isolated yield 19.0%), based on *c,c*-**10**. GCMS showed this peak to consist of two major isomers in a ratio of 1.75:1.0. Both isomers had mass spectra which indicated a parent mass of 162 and a base peak at *m/e* 82. The HRMS determination of the parent mass was 162.1412, calcd 162.1409. The ^1H NMR was consistent with a (1.75:1.0) mixture of the endo and exo stereoisomers **19** and **20**: ^1H NMR ($DCCl_3$) [6.45–6.3 (quartet, **20**) and 6.3–6.05 (quartet, **19**), 2 H (bicyclic olefin)], [5.6–5.0 (m, **19** and **20**), 2 H (exocyclic olefin)], [2.4–2.0 (m, **19** and **20**), 3 H (allylic methines)], [2.0–0.6 (br, **35** and **36**), 11 H; with 0.8 (d, **20** methyl attached to a saturated site on the exo face and 0.65 (d, **19** methyl attached to a saturated site on the endo face) in a ratio of 1:1]. The ^{13}C NMR of this mixture is interpreted as follows



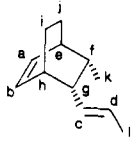
19



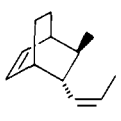
20

^{13}C NMR ($DCCl_3$) endo isomer **19**: (a) 133.5 (133.9), (b) 134.3 (133.9), (c) 134.3 (13691), (d) 122.7 (121.5), (e) 37.3 (31.0), (f) 38.0 (40.3), (g) 38.3 (51.6), (h) 26.9 (31.0), (i) 25.9 (29.0), (j) 19.0 (29.0), (k) 19.1 (21.7), (l) 13.4 (13.5). ^{13}C NMR ($DCCl_3$) exo isomer **20**: (a) 132.0 (134.3), (b) 135.4 (134.3), (c) 136.5 (136.1), (d) 124.6 (121.5), (e) 36.4 (31.0), (f) 37.0 (40.3), (g) 41.4 (51.6), (h) 36.0 (31.0), (i) 32.2 (28.6), (j) 19.9 (28.6), (k) 16.5 (21.7), (l) 13.2 (13.5).

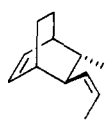
CRDA Reaction of 9 and *cis,trans*-2,4-Hexadiene (10). A solution containing 0.607 g (7.58 mmol) of **9** and 0.595 g (7.22 mmol) of *cis,trans*-2,4-hexadiene (**10**) (Albany International) in about 50 mL of dry methylene chloride was stirred at 0 °C in an ice bath. Then 0.419 g (0.513 mmol) or 7.11 mol % (based on *c,t*-**10**) of the aminium salt was added. Two collectable product peaks were observed to form by GC. The latter peak was the Diels–Alder dimers of **9** in 28.4% GC yield. The earlier product peak, containing **21**, **22**, and **23**, was formed in 24.5% GC yield (isolated 21.7%), based on starting *c,t*-**10**. GC/MS revealed that this first collected peak consisted of three separate isomers in a ratio of 1.0:2.9:2.3. Each compound afforded a parent peak at *m/e* 162 and a base peak at *m/e* 82 in the mass spectrometer. The HRMS on this mixture located a parent mass of 162.1405, calcd 162.1409. The NMR spectra were consistent with the assignment of **21**, **22**, and **23** to the isomers which eluted in order in a ratio of 1.0:2.9:2.3. ^1H NMR ($DCCl_3$) [6.30–6.05 (m, **21**, **22**, and **23**), 2 H (bicyclic olefin)], [5.65–5.15 (m, **21**, **22**, and **23**), 2 H (exocyclic olefin)], [2.6–2.0 (m, **21**, **22**, and **23**), 3 H (allylic methines)], [2.0–0.65 (br, **21**, **22**, and **23**), 11 H; 1.67 (d, **21**, methyl on trans double bond), 1.60 (d, **22** and **23**, methyls on cis double bond), 0.85 (d) and 0.71 (d), methyls attached to saturated sites]. The ^{13}C NMR was interpreted as the following



21



22

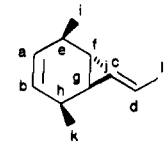


23

^{13}C NMR ($DCCl_3$) isomer **21**: (a) 133.2 (133.9), (b) 133.7 (133.9), (c) 135.0 (136.1), (d) 124.0 (121.5), (e) 26.2 (31.0), (f) 37.9 (40.3), (g) 47.8 (51.6), (h) 37.7 (31.0), (i) 25.5 (29.0), (j) 18.9 (29.0), (k) 18.6 (22.1), (l) 18.0 (18.8). ^{13}C NMR ($DCCl_3$) endo isomer **22**: (a) 132.0 (134.3), (b) 136.1 (134.3), (c) 137.2 (136.5), (d) 121.1 (121.5), (e) 36.0 (31.0), (f) 40.2 (40.3), (g) 44.9 (46.6), (h) 36.4 (31.0), (i) – (29.0), (j) – (28.6), (k) – (21.7), (l) – (13.8). ^{13}C NMR ($DCCl_3$) isomer **23**: (a) 132.7 (134.3), (b) 135.0 (134.3), (c) 136.1 (136.5), (d) 125.8 (121.5), (e) 32.7 (31.0), (f) 36.4 (40.3), (g) 42.3 (46.6), (h) 36.3 (31.0), (i) 17.7 (28.6), (j) 26.8 (29.0), (k) 19.7 (22.1), (l) 16.2 (13.8).

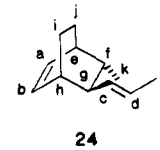
Cation Radical Catalyzed Isomerization of *cis,trans*-2,4-Hexadiene (10). A sample of 50 mg of *cis,trans*-2,4-hexadiene in 5 mL of dry methylene chloride at 0 °C was reacted with 20 mg of the aminium salt. The reaction mixture was allowed to stir for 5 min before quenching with 5 mL of methanol. A GC/MS analysis of the remaining 2,4-hexadiene (**10**) indicated that this sample now contained 3.78% of the trans,trans isomer, 95.50% of the cis,trans isomer, and 0.73% of the cis,cis isomer. An analysis of the starting *c,t*-**10** revealed the reagent to contain 1.24% of *t,t*-**10**, 98.76% of *c,t*-**10**, and no *c,c*-**10** by GC/MS. Thus the 2,4-hexadienes apparently undergo only minor rearrangement under CRDA conditions.

Thermal Diels–Alder Reaction of *trans,trans*-10 and 9. One gram each of 1,3-cyclohexadiene (**9**) and *trans,trans*-2,4-hexadiene (**10**) was sealed in a tube and heated at 210 °C for 36 h. Purification was performed by preparative GC and there were five resolvable peaks. GC/MS on the products of the first peak indicated that two isomers were present in a ratio of 1.68:1.0. The mass spectrum of both isomers contained a parent peak at *m/e* 164 and a base peak at *m/e* 82. The HRMS confirmed the parent mass at 164.1570, calcd 164.1565. The isolated yield of these two isomers was 33 mg (about 3%). The ^1H NMR supports the assignment of a syn and anti (1.68:1.0) pair of *trans,trans*-2,4-hexadiene (**10**) Diels–Alder homodimers. ^1H NMR ($DCCl_3$) 5.75–4.8 (m, 4 H, olefinic hydrogens), 2.3–1.2 (m, 4 H, methines), 1.65 (d, 3 H, methyl attached to a double bond), 1.1–0.65 (m of d, 9 H, methyls attached to saturated sites). The ^{13}C NMR was interpreted as follows



^{13}C NMR ($DCCl_3$) syn isomer: (a) 131.7 (133.9), (b) 132.1 (134.3), (c) 134.9 (135.7), (d) 125.4 (121.5), (e) 35.5 (46.5), (f) 36.8 (49.9), (g) 47.0 (61.5), (h) 34.7 (46.5), (i) 17.6 (20.0), (j) 17.6 (20.0), (k) 20.4 (22.5), (l) 16.0 (18.7). ^{13}C NMR ($DCCl_3$) anti isomer: (a) 131.3 (133.9), (b) 132.2 (134.2), (c) 134.5 (133.6), (d) 124.9 (121.5), (e) 35.7 (46.6), (f) 38.8 (49.9), (g) 48.3 (61.5), (h) 34.4 (46.5), (i) 20.1 (21.1), (j) 20.1 (21.1), (k) 18.2 (20.0), (l) 15.1 (15.1).

GC/MS on the products of the second peak indicated two isomers in a ratio of 1.0:2.7 were present. The total isolated yield collected was about 1% (12 mg). The mass spectrum of each stereoisomer contained a parent peak at *m/e* 162 and a base peak at *m/e* 82. The HRMS observed parent peak was 162.1412, calcd 162.1409. The ^1H NMR was very similar to that of the endo Diels–Alder adduct **18**; however, it was obvious that **18** was only a minor component. The exo Diels–Alder adduct **24** was the major isomer. ^1H NMR ($DCCl_3$) 6.35–5.85 (m, 2 H), 5.6–5.0 (m, 2 H), 2.3–1.9 (m, 3 H), 1.9–0.6 (br, 11 H) with 0.9 (d, **31**, methyl on exo face) and 0.7 (d, **37**, methyl on endo face) in a ratio of about 1:3. The ^{13}C NMR contained the peaks for **18**, and the remaining absorptions were assigned to the exo adduct **24**. ^{13}C NMR ($DCCl_3$) exo

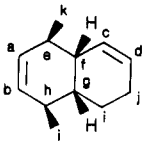


24

adduct **24**: (a) 132.2 (134.3), (b) 134.7 (134.3), (c) 135.7 (136.5), (d) 124.3 (121.5), (e) 36.8 (31.0), (f) 38.8 (40.3), (g) 49.8 (51.6), (h) 36.3 (31.0), (i) 26.7 (28.6), (j) 21.5 (29.0), (k) 18.2 (22.5), (l) 17.7 (18.8).

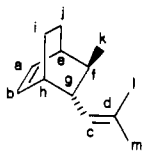
The total yield of product in the third collection was 20 mg or about 2%. GC/MS indicated that this peak corresponded to a single compound. The mass spectrum of this compound included a parent mass of 162 and a base peak at *m/e* 80. The HRMS located a parent mass at 162.1410, calcd 162.1409. The ^1H NMR is consistent with the exo Diels–Alder adduct formed in the reaction of *t,t*-**10** and **9**, but with **9** as the dienophilic component. ^1H NMR ($DCCl_3$) 5.9–5.2 (m, 4 H), 2.2–1.3

(br, 8 H), 1.0 (d, 3 H), 0.95 (d, 3 H). The ^{13}C NMR of this compound was analyzed as follows

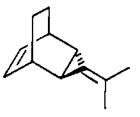


^{13}C NMR ($DCCl_3$) (a) 130.8 (132.3), (b) 130.2 (132.3), (c) 132.1 (132.3), (d) 126.5 (126.8), (e) 34.3 (46.0), (f) 37.8 (61.8), (g) 37.8 (58.0), (h) 35.3 (46.0), (i) 25.7 (35.2), (j) 25.4 (29.0), (k) 20.5 (22.5), (l) 21.8. The endo stereoisomer was also obtained in 2% yield.

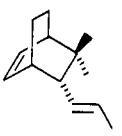
CRDA Reaction of 9 and *trans*-2-Methyl-2,4-hexadiene (11). To a 50-mL solution of 0.620 g (7.74 mmol) of **9** and 0.405 g (4.2 mmol) of *trans*-2-methyl-2,4-hexadiene (**11**) in dry methylene chloride at 0 °C was added 0.402 g (0.492 mmol) or 11.7 mol % (based on **11**) of the aminium salt. Two separate product peaks were observed to form by GC. The first peak, corresponding to the isomers **25**, **26**, and **27**, was formed in 92.6% GC yield based on starting **47**. The GC yield of the latter peak, the yield of dimers of **9**, was 26.8%. The initial peak had been determined by GC/MS to consist of three isomers in the ratio 1.17:5.45:1.0. The mass spectrum of each component of this GC collected peak contained a parent mass of 176 and a base peak at *m/e* 96. The HRMS confirmed the parent mass as 176.1568, calcd 176.1565. The olefin region of the ^1H NMR was instrumental in determining the identities of the various components. The large doublet at 4.8 and the smaller doublet at 4.6 indicated an endo/exo pair of adducts (**25** and **26**) in which the exo was the major isomer. The remaining small quartet at 5.15 in the exocyclic olefinic hydrogen region was assigned to **27**. The ^1H NMR of the major adduct formed was interpreted as follows



25



26

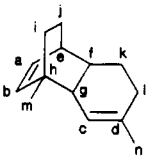


27

^1H NMR ($DCCl_3$) exo adduct **25**: 6.5–5.9 (m, 2 H, bicyclic olefin), 4.8 (d, 1 H, endocyclic olefin), 2.3–2.0 (m, 3 H, allylic methines), 2.0–0.8 (br, 5 H), 1.6 (s, 6 H, methyl groups attached to exocyclic double bond), 0.95 (d, 3 H, methyl attached to a saturated site and on the endo face). The ^{13}C NMR of this compound was interpreted as follows: ^{13}C NMR ($DCCl_3$) *exo*-**26**: (a) 132.2 (134.2), (b) 136.8 (134.3), (c) 131.8 (128.6), (d) 128.6 (129.0), (e) 26.9 (31.0), (f) 40.7 (40.3), (g) 46.5 (46.6), (h) 36.6 (31.0), (i) 19.0 (28.6), (j) 27.0 (29.0), (k) 18.2 (22.5), (l) 26.0 (26.5), (m) 18.0 (21.5).

Mixed Reactions between 1,3-Cyclohexadiene (9) and Diene 11. A solution of 0.114 g (1.43 mmol) of 1,3-cyclohexadiene and 0.124 g (1.29 mmol) of diene **11** in 2 mL of dry acetonitrile containing 0.041 g (0.32 mmol) of 1,4-dicyanobenzene was irradiated for 4.5 h. GC/MS analysis of the solution determined four components believed to be cross adducts were formed (12.6%:61.4%:15.5%:10.6%). The first two isomers showed a parent peak at *m/e* 176 and a base peak at *m/e* 96, whereas the latter two isomers showed no parent peak but showed a base peak at *m/e* 96. In addition, the Diels–Alder dimers and photodimers of **9** were present in comparable quantities (Diels–Alder dimers:photodimers = 1.3:1.0; dimers of **9**:cross adducts = 1.0:1.1). A control reaction showed a trace of the same cross adducts (11.4%:53.4%:16.8%:18.5%) as well as the photodimers of **9** in the usual ratio. In order to compare the ratios of cross adducts, a solution of 0.128 g (1.59 mmol) of **9** and 0.167 g (1.74 mmol) of **11** in 3 mL of dry methylene chloride was mixed with 0.061 g (0.074 mmol) of the triarylaminium salt. GC/MS analysis showed the same four cross adducts in similar ratio (12.9%:61.0%:14.5%:12.0%) as well as Diels–Alder dimers of **9** (cross adducts: dimers of **9** = 6.0:1.0).

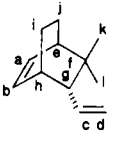
CRDA Dimerization of 1-Methyl-1,3-cyclohexadiene (12). To a solution of 0.521 g (5.54 mmol) of 1-methyl-1,3-cyclohexadiene in about 50 mL of dry methylene chloride at 0 °C was added 0.204 g (0.250 mmol) or 4.51 mol % of the aminium salt. A single peak was observed to form in the GC in 80.15% yield. The GC/MS indicates two stereoisomers in a ratio of 1.93:1.0, both with parent peaks of 188 and base peaks at *m/e* 94. The ^1H NMR is in excellent accord with only one set of endo/exo regioisomers, **28** and **29** (1.93:1.0). ^1H NMR ($DCCl_3$) [6.4–5.7 (m, **28** and **29**), 2 H], [5.4 (s, **28** and **29**), 1 H], [2.5–0.8 (br, **28** and **29**), 11 H], [1.7 (s, **29**) and 1.6 (s, **28**), 3 H], [1.15 (s, **28**) and 1.1 (s, **29**), 3 H]. The ^{13}C NMR was interpreted as follows



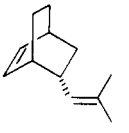
28(endo)
29(exo)

^{13}C NMR ($DCCl_3$) endo adduct **28**: (a) 133.2 (133.9), (b) 140.4 (141.4), (c) 137.6 (127.8), (d) 122.6 (126.3), (e) 27.2 (31.0), (f) 42.1 (40.3), (g) 45.1 (54.1), (h) 40.3 (35.6), (i) 30.2 (34.3), (j) 24.5 (26.8), (k) 37.9 (35.3), (l) 35.5 (34.1), (m) 26.8 (30.0), (n) 23.4 (26.3). ^{13}C NMR ($DCCl_3$) exo adduct **29**: (a) 135.7 (134.3), (b) 137.8 (141.8), (c) 135.0 (127.8), (d) 121.6 (126.3), (e) 28.6 (31.0), (f) 37.8 (40.3), (g) 45.0 (54.1), (h) 36.8 (35.6), (i) 28.3 (33.9), (j) 23.3 (26.4), (k) 36.2 (34.9), (l) 34.2 (34.1), (m) 27.7 (30.0), (n) 23.0 (26.3).

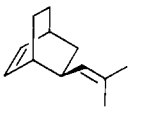
CRDA Reaction of 9 and 4-Methyl-1,3-pentadiene (13). A solution of 0.521 g (6.50 mmol) of **9** and 0.478 g (5.82 mmol) of 4-methyl-1,3-pentadiene (**13**) (Fluka A.G.) in about 50 mL of dry methylene chloride was stirred in an ice bath. Then 0.440 g (0.539 mmol) or 9.26 mol % (based on **13**) of the aminium salt was added. Two product peaks were observed to form by GC. The later peak was confirmed by GC/MS to contain only the dimers of **9**. GC/MS on the first peak collected (isolated yield of 25.2%) indicated that three isomers were present in a ratio of 1.1:3.35:1.1. Each had a parent mass of 162 and a base peak at *m/e* 82 in their respective mass spectra. The products were identified as **30**, **31**, and **32** on the basis of their NMR spectra and retention times on the GC/MS capillary column. In the ^1H NMR the methyl groups attached to double bonds (near 1.6) integrated less than those near 0.8 by about 2:3, indicating a chemoisomer similar to **31** as the major isomer. Since **30** and **32** were formed in approximately the same quantity, it was difficult to determine by NMR which isomer was the major chemoisomer of these two components. The assumption was made that the first compound to elute off the capillary column was the endo isomer. Thus the ratio of endo:exo (53.354) was assigned to the two peaks formed in a 1.1:1.0 ratio. The ^1H NMR was somewhat complex but still very indicative of Diels–Alder cycloadducts. ^1H NMR ($DCCl_3$) 2.6–2.1 (m, 3 H, allylic olefin), 4.8–4.35 (m, 2.2 H, exocyclic olefin), 2.6–2.1 (m, 3 H, allylic methines), 2.0–0.8 (br, 11 H); with 1.6 (s), 1.05 (s), and *x*0.95 (s) (2:3). The ^{13}C NMR of the major isomer was interpreted as follows



31



30



32

^{13}C NMR ($DCCl_3$) *endo*-**52**: (a) 132.3 (134.3), (b) 135.4 (134.3), (c) 149.1 (143.6), (d) 109.9 (114.0), (e) 35.7 (38.5), (f) 38.0 (44.9), (g) 54.9 (59.1), (h) 28.2 (31.0), (i) 19.1 (26.4), (j) 18.0 (26.4), (k) 23.4 (29.6), (l) 21.6 (29.6).

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