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THE CATION RADICAL VINYLCYCLOBUTANE REARRANGEMENT

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ABSTRACT

The cation radical vinylcyclobutane (VCB) rearrangement is found to be a reaction of substantial scope, synthetic utility, and exceptional kinetic facility. In conjuction with cation radical cyclobutanation, it constitutes an effective method for net (indirect) Diels–Alder addition to electron rich dienophiles. Reactions can be carried out with either aminium salt or photosensitized electron transfer (PET) initiation and are powerfully facilitated by ionizable substituents such as *p*-anisyl, phenylthio, and phenoxy at the 2-position of the vinylcyclobutane. The intramolecularity of the reaction is clearly established and in four discrete systems preferred sr (suprafacial/retention) stereochemistry is observed. A theoretical basis for sr stereochemistry in the cation radical VCB rearrangement is advanced. The transition state for the reaction is considered to be similar to that for the direct cation radical Diels–Alder cycloaddition, another cation radical pericyclic reaction which converges on the same product. This model of the VCB rearrangement transition state is used to rationalize the strong rate-retarding effect of a *Z*-methyl substituent attached to the vinyl group and of a methyl substituent at the 4-position of the vinylcyclobutane ring *cis* to the vinyl substituent.

INTRODUCTION

Cycloadditions involving olefinic and dienic cation radicals have already been shown to have tremendous kinetic impetus and are found to provide efficient and selective synthetic routes to three-, four-, and six-membered carbocycles.[1–7] Much less is known of other pericyclic reactions of cation radicals, but the encouraging prediction has been advanced that a wide range of pericyclic reaction types should be powerfully accelerated by ionization to the cation radical state.[8] One of the theoretical reaction path studies upon which this prediction was based involves the cation radical Cope reaction ([3,3] sigmatropic shift). An instance of this type of sigmatropic reaction has subsequently been observed.[9] Many examples of cation radical [1,3] sigmatropic shifts have been reported, but these almost exclusively involve matrix isolated cation radical *excited states*.[10–13] The present work focuses on ground state cation radical [1,3] sigmatropic shifts and, more particularly, on the vinylcyclobutane (VCB) rearrangement. The results, a brief and partial account of which has been published elsewhere,[14] provide strong confirmation of the predicted facility of cation radical sigmatropic shifts and imply potential synthetic utility for the reaction.

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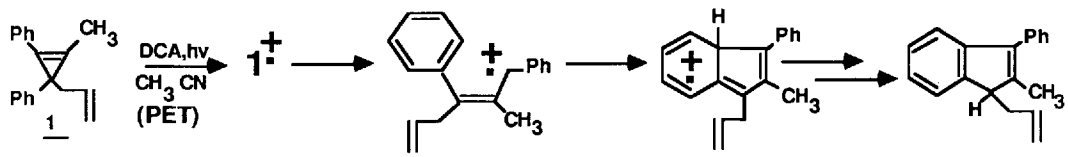
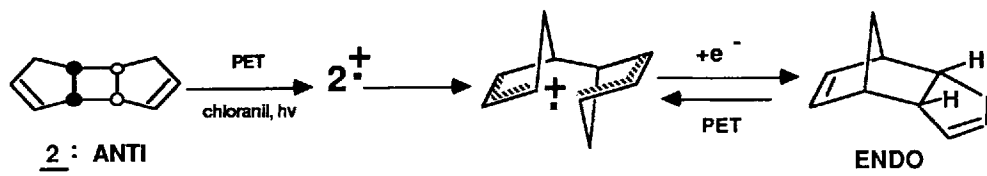
Historical precedents

Very few observations have been reported relevant to [1,3] sigmatropic shifts of carbon—carbon bonds of ground state cation radicals; however, the PET (photosensitized electron transfer) induced rearrangement of 3-phenylcyclopropenes to indenes (Scheme 1) may well be one such instance.[15] The tentative mechanistic proposal invokes a stepwise process involving cleavage to a carbene cation radical, followed by cyclization of the latter functionality to the *ortho* position of the 3-phenyl ring.



Scheme 1

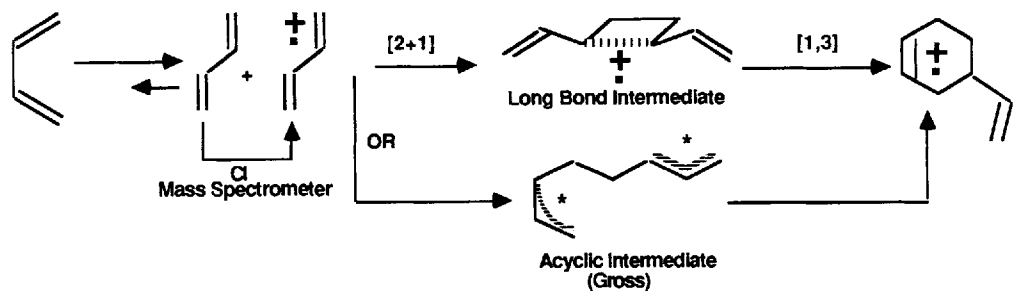
The cation radical vinylcyclobutane rearrangement has apparently also been observed (Scheme 2). CIDNP studies of the rearranged product have been interpreted to suggest a stepwise (non-pericyclic) mechanism.[16]



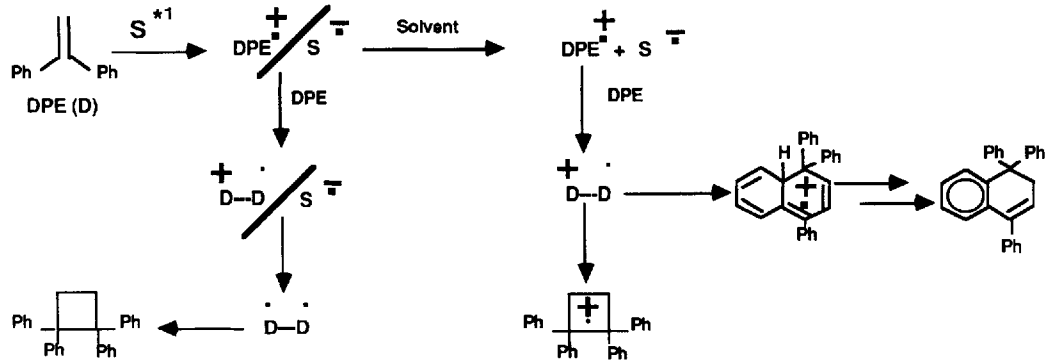
Scheme 2

In retrospect, two additional observations can also be considered as possible examples of cation radical [1,3] sigmatropic shifts of the VCB type. The reaction of the 1,3-butadiene cation radical with neutral 1,3-butadiene has been studied by MS/MS techniques and found to yield the 4-vinylcyclohexene (Diels–Alder adduct) cation radical.[17] However, since the diene exists principally in the s-*trans* conformation, the molecular ion must also be assumed to have this conformation. Reaction between the s-*trans* cation radical and the s-*trans* diene, of course, can not directly afford the Diels–Alder adduct. Further, since cation radical/neutral cycloadditions (either cyclobutanation or Diels–Alder addition) are predicted and found to have extraordinarily small activation energies,[18,19a] it is unlikely that conformational isomerization (*s-trans* to s-*cis*) in either the neutral or the cation radical could occur at a rate comparable to cycloaddition. Consequently, the cycloaddition which occurs is highly likely to be a cyclobutanation and the cycloadduct (at least initially) the 1,2-divinylcyclobutane cation radical (*cis* and/or *trans*). The latter could then undergo a rapid VCB rearrangement to the Diels–Alder (DA) adduct (Scheme 3).[19b]

Still more recently, a careful study of the cyclodimerization of 1,1-diphenylethene (DPE) has revealed that a mixture of CB and DA adducts are formed and, importantly, that the latter is formed exclusively from the separated $DPE^{+\cdot}$, while the former derives primarily from the geminate ion radical pair ($DPE^{+\cdot}/S^{-}$).[20] The mechanism proposed (Scheme 4) invokes competition between, on the one hand, reaction of the germinate ion pair with DPE to yield an acyclic dimer cation radical geminate pair (D_2^{+}/S^{-}) and, on the other hand, diffusional

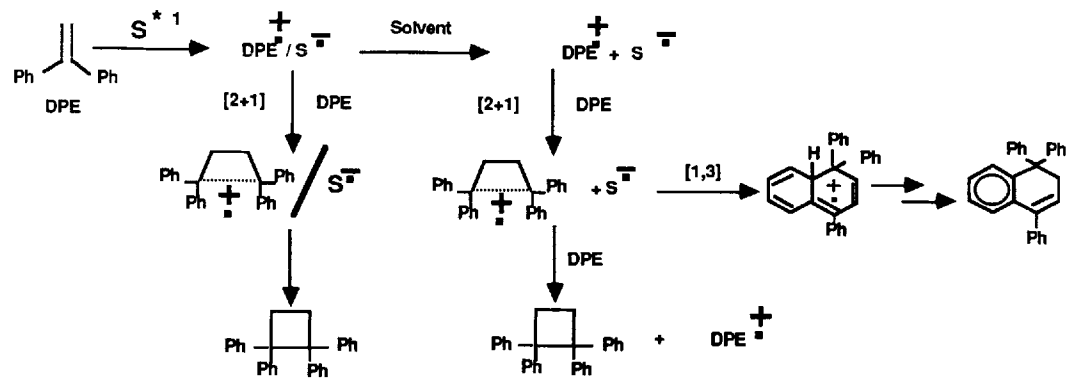


Scheme 3



Scheme 4

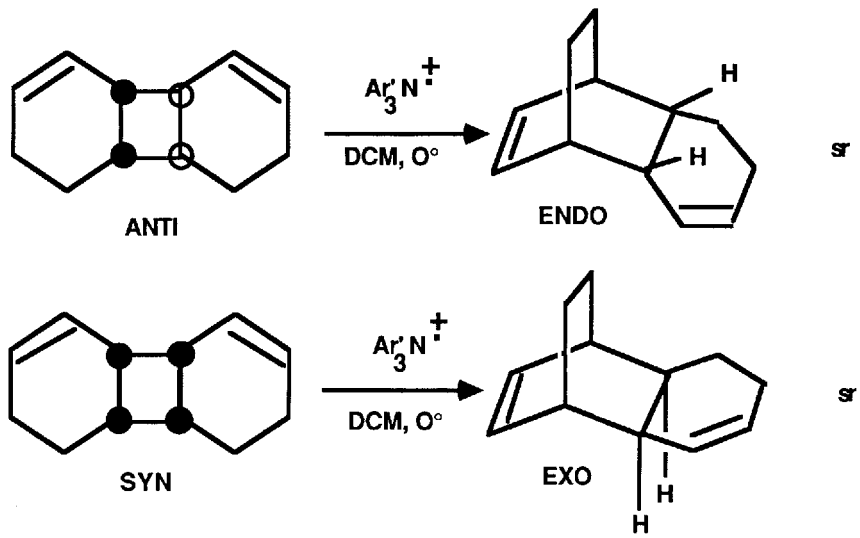
separation of the geminate ion pair (DPE^{+}/S^{-}) to separated ions (DPE^{+}), which then react with DPE to yield separated acyclic dimer cation radicals (D^{+}_{2}). The latter are considered to cyclize predominatly to DA adducts, but the geminate ion pairs undergo rapid back electron transfer to give an acyclic dimer diradical, which cyclizes exclusively to CB adducts. These important results appear to be equally consistent with a mechanism involving initial cyclobutanation (Scheme 5), followed by facile *phenylcyclobutane* rearrangement. The latter would be most likely for longer-lived CB cation radicals, i.e., those which have escaped the solvent cage. In accord with this general proposal, numerous examples of probable cation radical phenylcyclobutane to hydronaphthalene rearrangements have been proposed.[20b]



Scheme 5

RESULTS

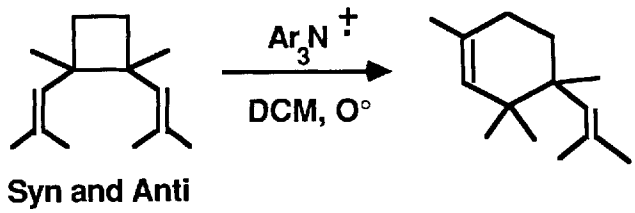
A mixture of the *syn*, *anti* cyclobutane (CB) dimers of 1,3-cyclohexadiene (CHD, from triplet sensitized dimerization, [21] Scheme 6) was initially subjected to attempted VCB rearrangement using the standard initiator system consisting of tris(4-bromophenyl)aminium hexachloroantimonate (Ar_3N^{+})/dichloromethane/O° C.[6] The cyclobutanes proved completely stable under these conditions. Since DA cyclodimerization of CHD occurs smoothly under just these



Scheme 6

conditions, this experiment nevertheless serves to confirm that the DA adducts are formed directly in this system, and not indirectly *via* the CB adducts. The large difference in the oxidation potentials of Ar_3N:(1·05V vs. S.C.E.[22]) and the CB adducts (>2·0V) suggests that the failure to observe the VCB rearrangement in this system may simply be the result of the inability of the aminium salt to generate the required VCB cation radicals. Consequently, the much more powerfully oxidizing aminium salt tris(2,4-dibromophenyl)aminium hexachloroantimonate[23] (Ar'_3N^{+}; $E_{1/2}$ = 1·47V vs. S.C.E.) was employed. Rearrangement to the corresponding DA adducts occurs within minutes at 0 °C when this initiator is used. An essentially pure (93%) sample of the *syn*-CB and a sample enriched in the anti-CB dimer (83%) were then obtained by preparative GC and rearranged individually. The reactions are both sr stereoselective, the *anti*-CB yielding essentially only the *endo*-DA adduct and the *syn*-CB yielding (±5%) only the *exo*-DA adduct. The experiment with the pure *syn* isomer is the more critical one, since the *exo*-DA isomer is produced only in very small quantities (4·5:1, *endo*:*exo*) in the aminium salt initiated cyclodimerization of CHD.[6] Consequently, a mechanism involving retrocyclobutanation/DA addition is decisively excluded.

The mixture of *syn*-, *anti*-CB dimers derived from the fluorenone triplet sensitized cyclodimerization of 2,4-dimethyl-1,3-pentadiene[24] (Scheme 7) rearranges quantitatively even using the milder aminium salt (Ar_3N^{+}). The DA adduct formed is constitutionally isomeric with that formed in the aminium salt catalyzed cyclodimerization of this diene.[25] Therefore, retrocyclobutanation/DA addition is again ruled out. The special ease of ionization of these

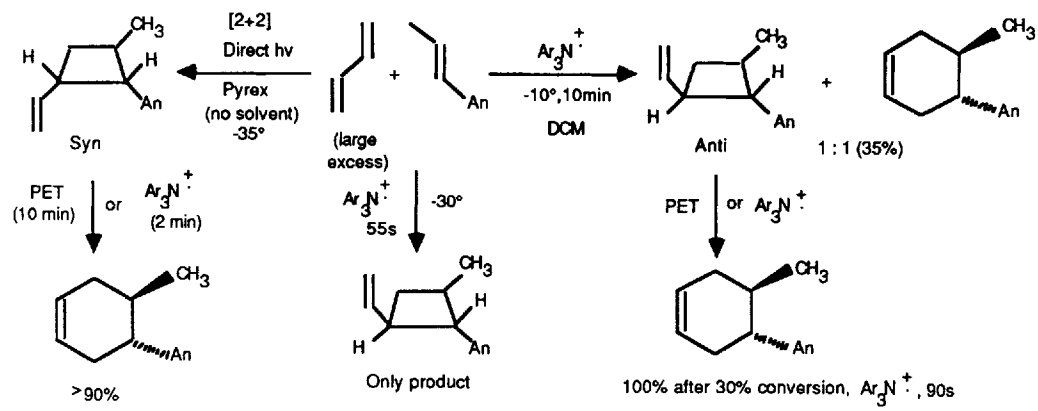


Scheme 7

CB's must derive in part from relief of steric repulsions in the 1,1,2,2-tetrasubstituted cyclobutane, but also in part from the stabilization of the resultant VCB cation radical by the numerous alkyl groups. More specifically, the suggestion is advanced that ionization occurs from the hindered sigma bond, thus permitting all of the alkyl groups to stabilize the resulting cation radical via the long bond structure.[26]

VCB rearrangement of 2-anisylvinylcyclobutanes

As would be expected, the presence of a *p*-anisyl group at the 2-position of a VCB greatly facilitates ionization to the VCB cation radical and makes feasible initiations via the milder aminium salt and by PET. The *syn* and *anti* isomers of Scheme 8 were prepared by distinct



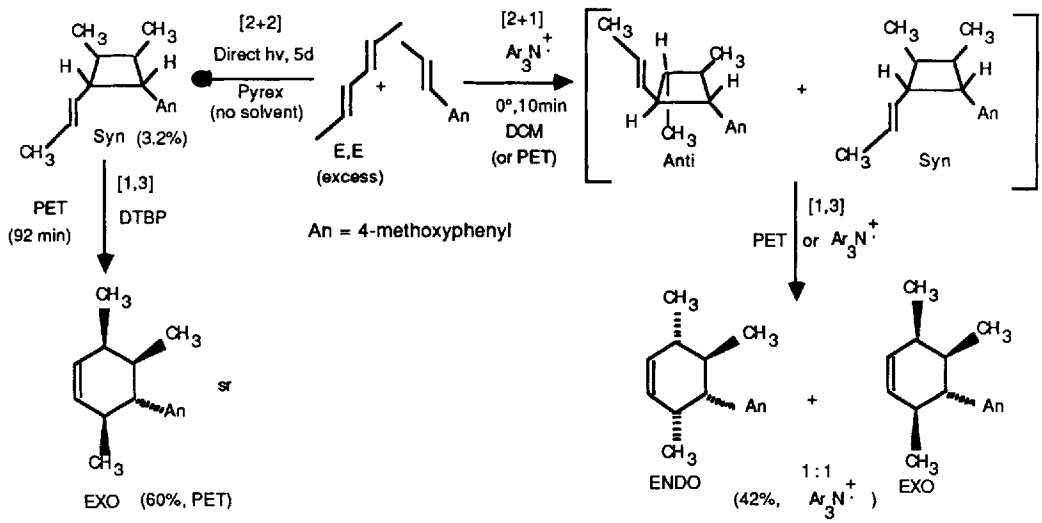
Scheme 8

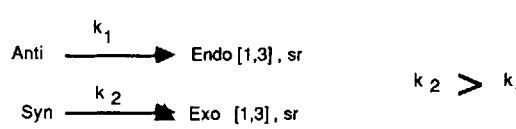
routes involving direct photoaddition of 1,3-butadiene and *E*-anethole via the exciplex (*syn*)[27] and cation radical cycloaddition (aminium salt) of these same two addends (*anti*).[28] Both stereochemistries have strong precendents from the methods of synthesis. In addition, the benzylic hydrogen of the *anti*-CB typically experiences a characteristic relative upfield chemical shift as a result of the anisotropy of the vinyl double bond. (This has been consistently observed in this laboratory when the alpha substituent is phenoxy, phenylthio, and N-methyl-N-acetamido). Rearrangement of both isomers to the same DA adduct occurs smoothly under either PET or aminium salt (Ar_3N^+) conditions. Added 2,6-bis(*tert*-butyl)pyridine, incidentally, has no effect on the results, thus excluding a Brønsted acid catalyzed mechanism.[29,14,25] Under PET conditions (100 mol% 1,4-dicyanobenzene ≡ DCB;

substrate, 100 mol%; acetonitrile, 0·13 M, pyrex, *hv*), the yield of DA adducts is quantitative up to at least 70% conversion, which is attained in only 10 mins of irradiation. Under aminium salt conditions ($Ar_3N^{\cdot+}$, 7·4 mol%; substrate, 100 mol%; dichloromethane, 0·12M; 0 °C, 2 min) the same reactions are quantitative up to at least 30% conversion. In both cases, attempts to carry out the reaction beyond about 80% completion results in extensive decomposition of both the CB and DA adducts. The mechanistic possibility of retrocyclobutanation/DA addition was investigated once more by trapping experiments in which an excess (800 mol%) of 2,3-dimethyl-1,3-butadiene (DMB) was included in the reaction mixture. The VCB rearrangement occurs normally and, despite the much greater (2·98:1) reactivity of the trapping diene than 1,3-butadiene toward the *E*-anethole cation radical, only slight traces (<1%) of the *E*-anethole/DMB cycloadduct were formed. Even these minute amounts appear to derive from traces of *E*-anethole present in the VCB substrates (cf. method of preparation).

Stereochemistry

The observation has been consistently made that the cation radical VCB rearrangements are intramolecular. Of further interest from both mechanistic and synthetic viewspoints is the reaction stereochemistry. Accordingly, the *syn*-CB cycloadduct of *E*-anethole and *E,E*-2,4-hexadiene was synthesized via direct (exciplex) photoaddition. The rearrangement of this CB under PET conditions is also extremely efficient (quantitative yield up to 85 % conversion, 30 min) and affords predominantly (7:1) the *exo* adduct, again via an sr stereochemical course (Scheme 9). Even the small amount of *endo* product obtained almost certainly arises from

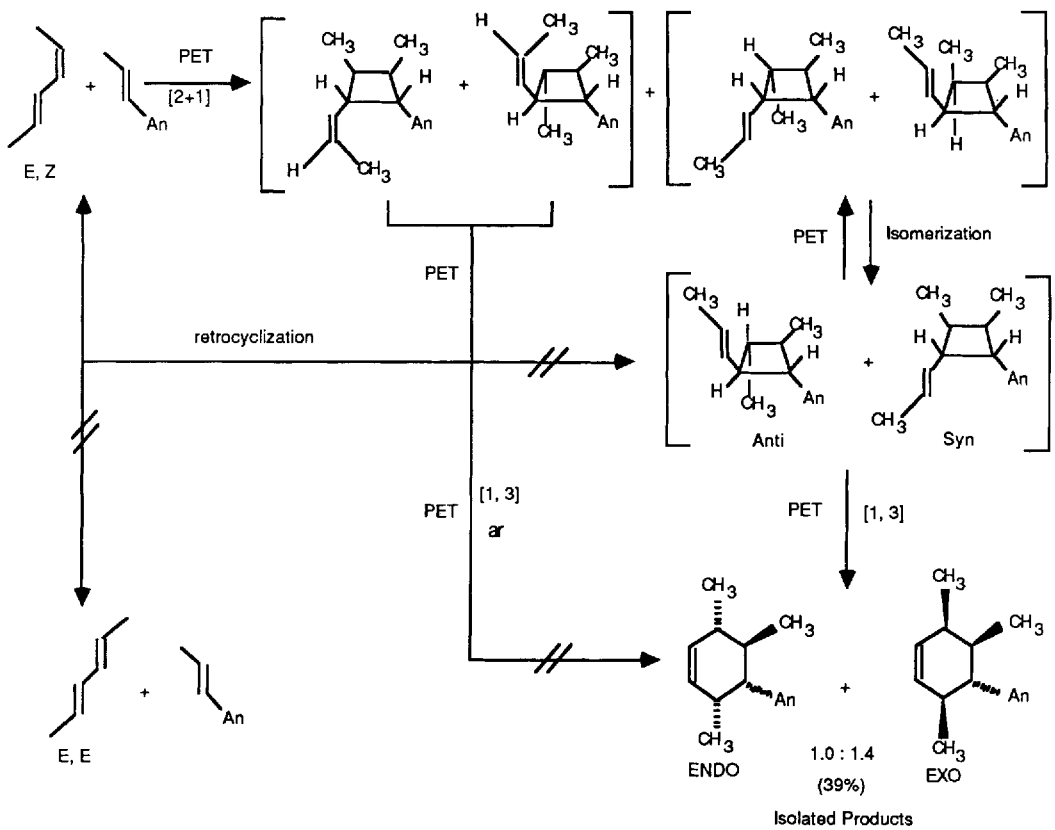




Scheme 9

impurities in the starting material, since this product cannot be obtained by any intramolecular VCB rearrangement. Consequently, the sr stereochemical preference must be essentially 100% in this system. The intramolecularity of the rearrangement was again decisively established by trapping experiments. In this case the trapping diene included in the reaction mixture was *trans*-1,3-pentadiene, a diene found to be 13·4 times as reactive as *E,E*-2,4-hexadiene toward the *E*-anethole cation radical. The rearrangement proceeded as in the absence of the trap, and cross adducts of *E*-anethole/*trans*-1,3-pentadiene were not observed in more than trace amounts.

The corresponding *anti*-VCB would ordinarily be accessed via the cation radical cycloaddition route, but proved inaccessible in this instance because of the incredibly rapid VCB rearrangement under the cation radical conditions. Initial exclusive cyclobutanation has also been established in the aminium salt initiated cycloaddition of *E*-anethole to 1,3-butadiene (−30 °C, 55 s). In this case, however, the CB adduct could be isolated from a synthetic run (−10 °C, 10 min) and fully characterized by NMR and mass spectrometry.[28] In either the PET or aminium salt (Ar_3N^{+}) initiated cycloaddition of *E*-anethole and *E,E*-2,4-hexadiene (Scheme 9), GC/MS investigation of the product composition at very short (on a synthetic time scale) reaction times ($Ar_3N^{\cdot +}$, 5s, −30 °C; PET, 5 min) reveals that the DA adducts ultimately formed are not the initial products. Instead, the adducts which appear first at very short times (5s) are isomeric with the known Diels–Alder adducts, and appear,



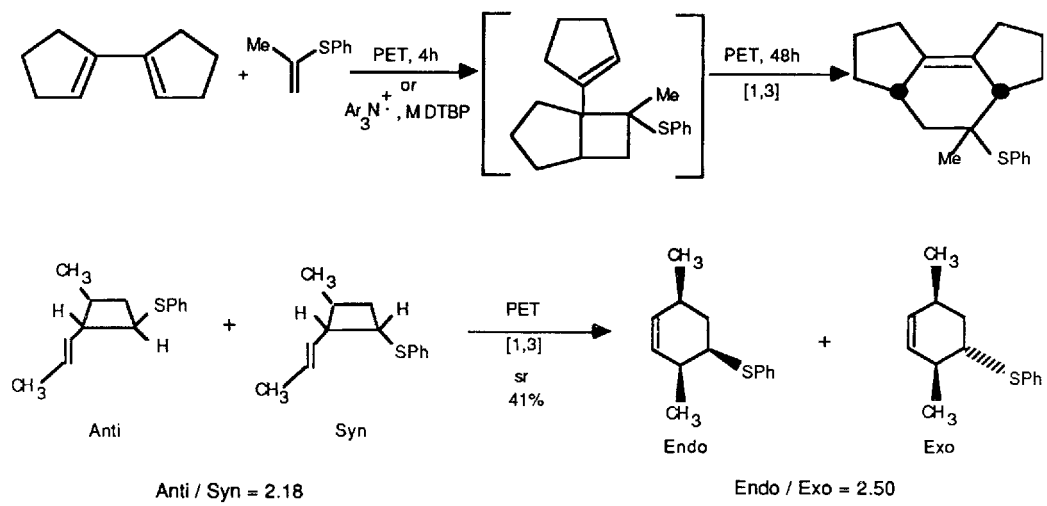
Scheme 10

according to the usual mass spectroscopic criterion to be CB adducts.[19] One of these CB adducts is presumed to be the unknown *anti*-CB adduct of interest, but the other, somewhat surprisingly, is not the known *syn*-CB isomer. The structure of this new isomer is presently unknown. At only slightly longer reaction times (15s) the *exo*-Diels–Alder adduct is the next detectable cycloadduct, followed (30s) by the known *syn*-CB adduct. At longer times, the *endo*-DA isomer finally appears. Apparently, the *syn*-CB, which has already been shown to rearrange to the *exo*-DA isomer, is much more susceptible to rearrangement than the *anti*-CB, and escapes detection for a time as the result of its very rapid rearrangement. All the CB intermediates very quickly begin to rearrange, at extremely low conversion, to the DA adducts (1:1, *endo*:*exo*). Since it has already been established that the *syn*-cyclobutane rearranges predominantly to the '*exo*'-Diels–Alder adduct, the *anti*-CB must presumably rearrange at least predominantly to the '*endo*'-DA adduct.

It is both interesting and instructive to compare the cycloaddition/VCB rearrangement of *E*-anethole and *E,E*-2,4-hexadiene with the corresponding reaction of *E,Z*-2,4-hexadiene. Whereas terminally *Z*-substituted dienes are notoriously slow to react via a direct Diels-Alder mechanism, *E,Z*-2,4-hexadiene reacts with *E*-anethole (PET conditions) at least as rapidly as does the *E,E* isomer. Further, the CB intermediates now persist much longer and are more numerous. Included among these CB adducts are the three formed in the reaction of the *E,E* isomer. Nevertheless, the only adducts present after a time are the same '*endo*' and '*exo*'-DA adducts (1·0:1·4) isolated from the *E,E* isomer (Scheme 10). That *E,Z* to *E,E* isomerization is not occurring during the reaction is indicated by analysis of the recovered diene after partial reaction. Thus, after 70% conversion, the recovered 2,4–hexadiene had an *E,Z*:*E,E* ratio of 96:4, as compared to the 97:3 ratio found for the starting diene.

VCB rearrangement of 2-(phenylthio)vinylcyclobutanes

Second only to the *p*-anisyl group in providing facilitation to the cation radical VCB rearrangement, as observed in this work, is the phenylthio substituent.[30] In the addition of phenyl propenyl sulfide to 1,1′-dicyclopentenyl (Scheme 11), cyclobutane adducts are again

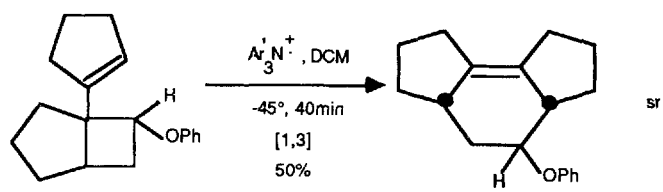


Scheme 11

detectable as the sole primary products at very short reaction times and low conversions. Very quickly, these primary products give way to the Diels–Alder adducts, strongly suggesting a facile VCB rearrangement. The extreme rapidity of the rearrangement again precludes isolation of the VCB adducts for independent study. However, the CB adducts of phenyl vinyl sulfide (PVS) and *E,E*-2,4-hexadiene are readily available from cation radical cycloaddition. The *anti* isomer predominates (2·18:1) in this product mixture. The *syn* isomer, however, is not available via direct exciplex addition. Rearrangement of the *anti* enriched mixture under PET conditions is quite facile (78% conversion in 20 min) and produces preponderantly (3:1) the '*endo*' adduct, again via an sr stereochemical course (Scheme 11). In this instance, the trapping experiments which demonstrate intramolecularity utilize the triene 1-ethenyl-4-(2-propenyl)cyclohexene as a reactive trap. This triene has previously been found to react extremely efficiently with the phenyl vinyl sulfide cation radicals which would presumably be produced in a retrocyclobutanation reaction (the $E_{1/2}$'s are 1·42 and 1·59 for PVS and *E,E*-2,4-hexadiene, respectively). Quantitative competition experiments reveal that the relative reactivities of the trap and *E,E*-2,4-hexadiene toward PVS^{+} are in the ratio 1:2·2. When the rearrangement is carried out in the presence of the trap, no cross adducts of PVS with the trap could be detected by GC/MS. Similarly, N-methyl-N-vinylacetamede (MVA) is an excellent trap for *E,E*-2,4-hexadiene cation radicals. If any of the 2,4-hexadiene cation radicals are formed via retrocyclobutanation, cross adducts with MVA would be observed. In fact, the rearrangement occurs normally in the presence of MVA, and no cross adducts with MVA are formed.

VCB rearrangement of a 2-(phenoxy)vinylcyclobutane

The cation radical cross cycloaddition of 1,1′-dicyclopentenyl and phenyl vinyl ether (PVE) has previously been shown to yield predominantly (82%) CB adducts.[30] The cation radical VCB rearrangement (Scheme 12) of this *syn*, *anti* (7:1) adduct pair is inefficient, in a synthetic sense, where either of the aminium salts is employed at 0 °C (Scheme 12). With Ar_3N^{+}, for



Scheme 12

example, smaller amounts of the initiator (5–10 mol%) effect only modest conversions (40–60%) to DA adducts. Consequently, though yields (based on starting materials consumed) are good (>80%), the product is typically a *ca.* 2:1 DA:CB mixture. When larger amounts of this initiator are used (10–20%), the CB's are completely consumed but yields drop precipitously because of product decomposition. A highly effective solution to this dilemma was developed which uses Ar'_3N^{+} at −45 °C. The more conventional aminium salt (Ar_3N^{+}), incidentally, is too insoluble in dichloromethane for use at these low temperatures. Under the revised conditions, complete conversions of CB to DA adducts is achieved in high yield (67%; 50% isolated). For best yields, the initiator is added (as the solid) in small (*ca.* 2·5

mol%) portions at intervals of 1–2 minutes until a total of 20 mol% has been added or, even better, until GC monitoring indicates an appropriate level of conversion. This procedure may well represent the optimum one for synthetic exploitation of the cation radical VCB rearrangement, generally, since the DA adducts appear to be rather stable under these conditions. Especially significant, in the context of the present reaction, is the fact that in this system the *syn*-CB is the predominant isomer, and that it rearranges preferentially to the *exo*-DA adduct, but again via sr stereochemistry. In this single instance, decisive confirmation of the intramolecularity of the VCB rearrangement could not be obtained. The powerful initiator $Ar_3'N^{+\cdot}$ is capable of ionizing any of the potential trapping molecules, thus causing destruction of the trap and inhibition of the rearrangement.

Rate retardation by addends

It is a matter of some curiosity that VCB's can be prepared under cation radical conditions which formally ($Ar_3N^{+\cdot}$ or PET) are the same as those subsequently used to bring about efficient VCB rearrangement. The basis for this anomaly appears to be the presence, under cycloaddition conditions, of substantial concentrations of the ionizable addends. The latter, being usually far more ionizable than the VCB adducts, suppress the formation of VCB cation radicals and therefore strongly suppress the VCB rearrangement. The complete removal of these addends is therefore an essential aspect of the purification of the VCB adducts in preparation for the VCB rearrangement. Strong rate retardation by added *E*-anethole (Schemes 8 and 9), PVS (Scheme 10), and 1,1'-dicyclopentenyl (Scheme 11) have, for example, been established under both aminium salt and PET conditions. The unusual aspect of the additions involving *E*-anethole is that, under cycloaddition conditions even in the presence of a large excess of the highly ionizable substrate *E*-anethole the initially produced CB adducts quickly start to rearrange to DA adducts. Apparently, these CB adducts are substantially more ionizable than the other CB adducts studied, and/or the 2-anisyl group is uniquely effective in accelerating the VCB rearrangement. Consequently, we originally failed to detect the formation of these CB adducts.[28]

DISCUSSION

The cation radical VCB rearrangement emerges as extremely facile in a variety of cases when ionization to the VCB cation radical is provided. The electron transfer whereby the latter is formed need not be, and perhaps preferably is not, exothermic. In fact, facile reactions are observed when this electron transfer is endothermic by as much as 0·5V. However with less ionizable, hydrocarbon, VCB substrates a powerful electron acceptor such as tris (2,4-dibromophenyl) aminium hexachloroantimonate ($Ar_3'N^{+\cdot}$) may be required in order to maintain the endothermicity at or below this level. The presence of readily ionizable substituents at the 2-position of the VCB provides ionization under milder conditions, including both tris(4-bromophenyl) aminium hexachloroantimonate ($Ar_3N^{+\cdot}$) and PET initiators. These substituents include *p*-anisyl, phenylthio, and phenoxy. In related work, the less readily ionizable substituents ethoxy and N-methyl-N-acetamido have been found not to induce facile VCB rearrangement. An effective synthetic procedure for achieving complete conversion of CB to DA adducts in high yields appears to be available in the $Ar_3'N^{+\cdot}$/−45 °C/dichloromethane procedure.

Cation radical mechanism

Mechanistically the VCB rearrangements are decisively characterized as occurring via cation radicals by the observation that they occur under both PET and aminium salt conditions and with analogous stereochemical results.[25] *Brønsted acid catalysis* is specifically excluded by the observation that hindered pyridine bases do not suppress or even strongly affect the majority of the reactions.[29,14,25]

Intramolecularity

The intramolecularity of these reactions is also confirmed and retrocyclobutanation/DA addition excluded by means of several discrete criteria. The stereospecificity embodied in Schemes 6 and 9 is, of course, inconsistent with the retrocycloaddition mode. Stereoselective formation of the *exo*-DA dimer of CHD from the *syn*-CB dimer (Scheme 6) is particularly decisive, since the aminium salt-initiated cation radical DA cyclodimerization of CHD yields predominantly (5:1) the *endo* adduct.[6] Similarly, the cycloaddition of *E,E*-2,4-hexadiene and *E*-anethole eventually yields a 1·0:1·0 *endo*:*exo*-DA mixture, while the VCB rearrangement of the *syn*-CB adduct (Scheme 9) yields mainly the *exo* adduct. The aminium salt-initiated cyclodimerization of 2,4-dimethyl-1,3-pentadiene actually yields a different constitutional isomer than that obtained in the VCB rearrangement of the CB (triplet) dimer. Intramolecularity is clearly established in the rearrangement of the *E*-anethole/1,3-butadiene and *E*-anethole/*E,E*-2,4-hexadiene CB cycloadducts by *in situ* trapping experiments.
Retrocyclobutanation should produce the appropriate diene along with the *E*-anethole cation radical. Inclusion in the reaction medium of an appropriate trapping diene which is, preferably, more reactive towards the *E*-anethole cation radical than is the diene produced by retrocyclobutanation should result in the formation of cross adducts between *E*-anethole and the trapping diene and at least partial inhibition of any rearrangement proceeding via a retrocyclobutanation/Diels–Alder addition mechanism. In the case of the 1,3 butadiene adduct, the trapping diene is 2,3-dimethyl-1,3-butadiene (reactivity toward *E*-anethole^{+} versus 1,3-butadiene, 2·98:1). Not even traces of the known[28] cross adduct involving the trapping diene and *E*-anethole are formed, and the rearrangement proceeds normally. In the case of the *E,E*-2,4-hexadiene adduct, the trapping diene is *E*-1,3-pentadiene (relative reactivity 13·4:1 versus *E,E*-2,4-hexadiene towards *E*-anethole^{+}). For the phenyl vinyl sulfide/*E,E*-2,4-hexadiene adduct, two discrete trapping procedures were used. In one case, the trapping diene 4-isopropenyl-1-vinylcyclohexene was used. The very slightly decreased reactivity of this trap toward PVS^{+} versus *E,E*-2,4-hexadiene (0·5:1·0) should be easily offset by the much greater concentration of the trapping diene than any diene generated by retrocyclobutanation. Again, not even traces of cross adduct involving the trap are found. In the second type of trapping experiment, N-methyl-N-vinylacetamide (MVA), an excellent caticophile for *both* the PVS and *E,E*-2,4-hexadiene cation radicals was used as the trapping agent. Identical results were observed. In only one case, the rearrangement of the phenyl vinyl ether/1,1′-dicyclopentenyl adduct, was a definitive trapping experiment not accessible. In this case, the extremely high reactivity of the $Ar_3'N^{+}$ initiator caused ionization of the various traps investigated, completely decomposing them and preventing consummation of the valid trapping experiment.

Stereochemistry

The stereochemical results for four distinct systems (Schemes 6, 9, 11 and 12) reveal a consistent preference for sr (suprafacial/retention) stereoselectivity. The results in the CHD dimer system (Scheme 6) are inherently less informative in regard to stereospecificity than those for the acyclic systems, since the rigidity of the former system effectively precludes both antarafacial and invertive stereochemical elements. This reservation does not apply to the three acyclic systems, of course. Of these latter systems, the most definitive results derive from the rearrangement of the *E*-anethole/*E,E*-2,4-hexadiene adducts (Scheme 9), in which case the stereospecificity is essentially 100%. The PVS/*E,E*-2,4-hexadiene (Scheme 11) and PVE/1,1′-dicyclopentenyl adducts (Scheme 12) rearrange with net sr stereoselectivity but the extent of the sr stereochemical preference is considerably less clear, since CB adduct mixtures were employed in both of these cases. Stereospecificity (as opposed to stereoselectivity) is therefore not demonstrated. The stereospecificity of the *E*-anethole/*E,E*-2,4-hexadiene adduct rearrangement strongly suggests a concerted process with preferred sr stereochemistry. The remaining results all appear, because of the consistent sr stereochemistry observed, to be consistent with the generalization of a concerted sr cation radical VCB rearrangement and thus is the tentative interpretation adopted here. Nevertheless, it is possible that the PVS and PVE adduct rearrangements have a significant stepwise, non-stereospecific component. This possibility will be investigated in future work.

Using a straightforward application of Woodward and Hoffman's 'HOMO' approach, which was originally applied to electrocyclic reactions, it has been predicted that [1,3] sigmatropic shifts of ground state cation radicals should occur preferentially with si (suprafacial/inversion) or ar (antarafacial/retention) stereochemistry.[31] This simple approach has previously been found inadequate for doublet pericyclic reactions,[32,33] and the generation of an erroneous prediction in the present instance is therefore not surprising. The experimental results are, however, in excellent accord with the extensive observations in the field of cation radical cycloadditions that allowedness/forbiddenness is, at most, of marginal significance.[14] More specifically, even forbidden pericyclic reactions such as cation radical cyclobutanation[8] often proceed with the negligibly small activation energies.[19] It appears logical to assume that, for cation radicals, that path should be preferred which most efficiently synchronizes the development of overlap in the bond being formed with the attenuation of overlap in the bond being broken, irrespective of aromaticity/antiaromaticity considerations. Intuitively, for a small cyclic system, this appears to be the sr path, since the introduction of antarafacial or invertive elements in such systems typically disrupts efficient cyclic conjugation. The [1,3] sigmatropic shifts of ground state singlets are also formally allowed in the si and ar modes and forbidden in the sr and ai modes. Nevertheless, violations of orbital symmetry (viz. sr stereochemistry) are common even in this area (neutral ground states) where aromaticity/antiaromaticity distinctions are most clearly drawn.[34] When the electron donor or acceptor substituents are attached to the migrating single carbon atom, a still further weakening of the orbital symmetry preference has been predicted.[35]

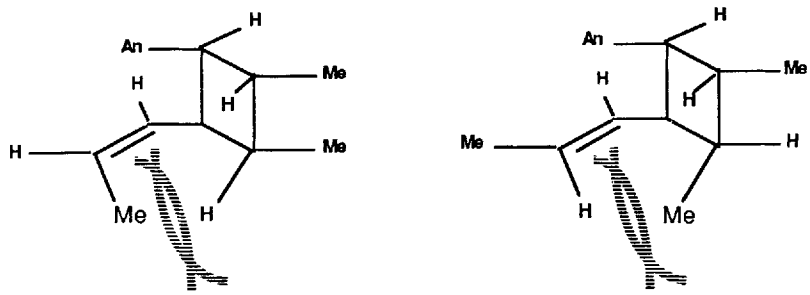
***Cis–trans* isomerizations**

The sr stereochemical outcomes discussed above are not formally observed in the rearrangement of the adducts of *E,Z*-2,4-hexadiene and *E*-anethole, since the eventual products are the same *endo*-, *exo*-DA adducts obtained from *E,E*-2,4-hexadiene. However, the early studies show that geometric isomerization of the initial CB aducts from

E,Z-2,4-hexadiene also yields the two CB adducts directly derived from the *E,E* isomer. The kinetic studies clearly reveal that the latter CB adducts rearrange much more rapidly to DA adducts than do those formed directly from the *E,Z* isomer. Consequently, the VCB rearrangement should still be considered as proceeding with sr stereochemistry. Geometrical isomerization of 1,2-disubstituted cyclobutanes under PET conditions is incidentally, well established.[36]

Transition state model for the cation radical VCB rearrangement

The circumstance that all four of the CB adducts directly derived from *E,Z*-2,4-hexadiene rearrange very much more slowly than either of those from the *E,E* isomer is quite interesting and suggests a transition state model for the cation radical VCB rearrangement which may have implications for VCB rearrangements of other mechanistic types. The model is specifically suggested by the fact that the net stereochemistry of the indirect Diels–Alder addition of *E*-anethole to *E,E*-2,4-hexadiene is identical to that expected for a direct Diels–Alder reaction between these two substrates (doubly suprafacial) and that, apparently the CB adducts directly derived from *E,E*-2,4-hexadiene are converted to DA adducts more rapidly than those from *E,Z*-2,4-hexadiene. These observations suggest the possibility that the transition state for the cation radical VCB rearrangement may indeed be very similar to that for a direct cation radical Diels–Alder addition leading to the same product. This would, for example, nicely explain the rate retardation engendered by the *Z*-methyl group on the propenyl double bond of one set of CB isomers obtained from *E,Z*-2,4-hexadiene (Scheme 13) and also the retardation by a *cis*-methyl group at the 4-position of the other set of isomers.



Scheme 13

Both of these methyl groups are analogous to a *Z*-methyl group on the terminus of the diene in a Diels–Alder addition. The effect of the *cis* 4-methyl substituent is perhaps less obvious than of the *Z*-propenyl groups, but is nevertheless of quite analogous origin, as may be seen from an examination of the s-*cis* vinylcyclobutane conformation required for rearrangement (Scheme 13). Presumably both effects are steric in nature. Previous results involving the *E*-anethole CB adducts of 4-methyl-1,3-pentadiene and *E*-2-methyl-2,4-hexadiene demonstrate the difficulty of rearrangement to a vinyl terminus bearing a *Z*-substituent.[28] Analogous results are obtained in the thermal rearrangement of 1,2-bis(propenyl) cyclobutanes.[37]

Reaction Path Details

A theoretical reaction path calculation for the prototype cation radical VCB rearrangement using an extended (3-21G) basis set *ab initio* SCF MO approach is currently being carried out and will be reported separately.[38] The results will confirm a minimal activation energy for the rearrangement and are in accord with the concerted path proposed here on the basis of the stereochemical results. Analogous experimental and theoretical results have previously been presented for the cation radical Diels–Alder reaction.[6,18] The correspondence of the results for these two closely related pericyclic reactions of cation radicals is highly encouraging. Moreover, for both of these reactions the conclusions of this research group relative to concertedness differ rather sharply from those of several other groups which postulate (for systems different from the ones of this study) a singly-linked, acyclic cation radical intermediate.[16,17] That mechanistic diversity might exist for cation radical pericyclic reactions for which activation energies are so miniscule is. of course, eminently reasonable. However, it should be noted that CIDNP results,[16] which have a very acute window of vision for intermediates of lifetime *ca.* 10^{-9}s, do not establish what fraction of the total product derives from such intermediates. More importantly, if intermediates are indeed predominantly involved in the systems studied by Roth and the others, the distinct possibility exists that they should be properly formulated as long bond structures or as ion-dipole complexes which retain stereochemical integrity. These quasi cyclic structures, incidentally, could be related to either the CB or DA adduct structure,[26] but might still have a predominantly bis(allylic) character.

Direct vs. indirect cation radical Diels–Alder

The emergence of the cation radical VCB rearrangement coupled with facile cation radical cyclobutanation of electron rich alkenes and styrenes by many acyclic conjugated dienes constitutes an indirect synthetic route for net Diels–Alder addition to electron rich dienophiles. In cycloadditions in which *E*-anethole or 4-vinylanisole is one of the addends, the VCB rearrangement is so facile that the indirect Diels–Alder becomes a 'one pot' reaction. In such circumstances the indirectness of the reaction is not necessarily apparent unless reaction mixtures are examined at quite early times. In most of the examples involved in the present work, execution of the cation radical VCB rearrangement requires removal of the ionizable addends. The question does arise, however, of whether, in still other instances, facile VCB rearrangements are capable of masking cyclobutanation and presenting the formal appearance of direct Diels–Alder addition. Direct DA additions are, of course, confirmed for the cyclodimerization of CHD through early time studies and the observation of stability of the CB adducts under cycloaddition conditions. Numerous other instances of exclusive direct cation radical cycloadditions have been confirmed in this laboratory by one or both of these criteria. In several cases, however, it does appear that the direct and indirect mechanisms are competitive. These latter include the cyclodimerization of such acyclic dienes as 1,1′-dicyclopentenyl and 2,4-dimethyl-1,3-pentadiene.

EXPERIMENTAL SECTION

Instrumentation

Routine ^{1}H-NMR and ^{13}C-NMR spectra were recorded on the following instruments: 500 MHz — General Electric GN-500 FT spectrometer; 360 MHz — Nicolet NT-360; 200 MHz —

Nicolet NT-200; 90 MHz — Varian EM 390 spectrometer; 80 MHz — Varian FT-80A Spectrometer. All samples were disolved in $CDCl_3$ or CS_2. All chemical shifts δ and coupling constants J are reported in ppm (relative to a tetramethylsilane 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 GOW MAC series 550P instrument equipped with a thermal conductivity detector (GC/TC) 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. Preparative GC was performed on the GOW MAC with a 5 ft × 1/4 in stainless steel column containing 10% SE-30 on Chromosorb W, HP (60–80 mesh). Capillary gas chromatographic analyses was performed with a Varian Model 3700 gas chromatograph with a flame ionization detector (GC/FI) on a 25 m SE-30 coated capillary column using N_2 as the carrier gas in conjunction with a Varian SP4270 integrator. Gas chromatograph-mass spectral (GC/MS) data were recorded with a Finnigan 4023 mass spectrometer with a 50m DB-1 (0·25 μ film) capillary column and are presented as *m/e* (% relative intensity). The GC/TC and GC/MS 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 the Aldrich Company and were used without further purification. Aminium salt reactions were carried out in dry dichloromethane (DCM distilled from phosphorous pentoxide). Tris (4-bromophenyl)aminium hexachlorantimonate (the aminium salt; Aldrich) was washed thoroughly with anhydrous ether and then dried *in vacuo* prior to use. Alternately, tris (2,4-dibromophenyl)aminium hexachloroantimonate[39] was elected in low temperature experiments or those where greater ionizing power was required. Typically, an appropriate amount of aminium salt was added (in DCM solution via syringe unless otherwise noted) as rapidly as possible to a cooled, magnetically stirred DCM solution of the appropriate substrate or substrates, with or without added di-*tert*-butylpyridine (DTBP) or 4-methyl-2,6-di-*tert*-butylpyridine (MDTBP). Usually after no more than 10 min., the reaction was quenched by the addition of a saturated methanolic solution of potassium carbonate, yielding a pale yellow solution (the aminium salt solutions are blue). The resulting mixture was then diluted with pentane (3–4 volumes), filtered, washed with water and then brine, dried by passing the solution through cotton or over magnesium sulfate and concentrated on a rotary evaporator. The residue was decanted from any precipitated tris (4-bromophenyl) amine (TBPA) and then purified by column chromatography (silica gel, 60–200 mesh) or thick layer chromatography (silica gel, 2000μ; Analtech), often followed by distillation.

In the PET procedure, HPLC grade acetonitrile was distilled from phosphorous pentoxide and, preferably, used freshly. Storage over molecular sieves (2Å) appears acceptable for limited periods (days). The sensitizer (1,4-dicyanobenzene ≡ DCB) was recrystallized from benzene. Reactions were typically run in 100 ml pyrex test tubes, de-gassed with dry nitrogen and sealed with a rubber septum and then aluminum foil. The reactions are sensitive to atmospheric moisture, but apparently not to atmospheric oxygen. The tubes were placed in a cool water bath against the outside of the cooling jacket of a medium pressure mercury vapor lamp. After completion of the irradiation period, the solvent was removed by rotary evaporation and the precipitated DCB by filtration. Further purification proceeds as in the aminium salt case.

Reaction of the triplet derived 1,3-cyclohexadiene dimers with $(2,4\text{-}Br_2Ph)_3NSbCl_6$ in the presence of DTBP

To a 25 ml round bottom flask was added 201 mg (1·26 mmol) of 3 CHD dimers[21] (*exo*-DA: 22·6%, *anti* CB: 58·23%, *syn* CB: 19·17%) formed under triplet conditions [irradiation of neat CHD with 2-acetylnaphthalene followed by chromatography (silica gel, pentane) then distillation (60 °C, 1 torr)], 149 mg (0·78 mmol) of DTBP, 225 mg (1·26 mmol) of phenanthrene (internal standard), and 7·5 ml of DCM. After cooling to 0 °C and while stirring, 685 mg (0·651 mmol) of $(2,4\text{-}Br_2Ph)_3NSbCl_6$ in 7.5 ml of DCM were added as rapidly as possible. The reaction was quenched with methoxide after 7 min. GC/MS analysis of the product solution revealed the *endo*-, *exo*-, *anti*-, and *syn*-CHD dimer isomers in a 39·45:33·83:18·4:8·31 ratio. The GC/MS revealed that 74·4% of the original material (all isomers) remained.

PRODUCT COMPOSITION %

Dimer	Before Reaction	After Reaction	After−Before(Δ)
endo-DA	0	39·45	39·45
exo-DA	22·6	33·83	11·23
anti-CB	58·23	18·4	−39·83
syn-CB	19·17	8·31	−10·86

The $|\Delta\ endo| \approx |\Delta\ anti|$ and the $|\Delta\ exo| \approx |\Delta\ syn|$. Although not definitive, these facts suggested that the *anti* and *syn* isomers were being converted directly and exclusively into the *endo* and *exo* dimers, respectively. Also implied is that all 4 isomers are equally susceptible to degradation, so that the product composition analysis can be handled as if the yield of the reaction was quantitative. The product distribution which would emerge from an alternative pathway, retrocyclization then DA recombination, can be quantitatively predicted since the ΔCB ($\Delta anti + \Delta syn$) and the expected product ratio (*endo*/*exo* = 4·56) from the aminium salt dimerization of CHD are known. The ΔCB = −50·69. For the proposed scenario, −ΔCB = ΔDA and *endo*/*exo* = 4·56. Thus, ΔDA = 50·69 = 40·552 + 10·136 and 40·552/10·135 = 4·56.

IF RETROCYCLIZATION THEN DIMERIZATION

Isomer Distribution	Before reaction	Predicted Change	Predicted Product
endo	0	0 + 40·552	40·552
exo	22·6	22·6 + 10·138	32·738
anti	58·23	observed	18·4
syn	8·31	observed	8·31

Comparing the predicted distribution with the observed (see first Table), it can be seen that the actual product distribution can be explained crudely by both alternative mechanistic schemes. This coincidence left further study necessary. The products' identities were affirmed by GC/MS wherein each isomer had a $M^+ = 160$ and a base peak = 80.

Reaction of *syn*-cyclobutane enriched 1,3-cyclohexadiene dimers with $(2,4\text{-}Br_2Ph)_3NSbCl_6$ in the presence of a hindered amine base

To a small vial was added *ca.* 10 mg (0·062 mmol) of 4 isomeric CHD dimers [*endo*: 2·00%, *exo*: 10·11%, *anti*: 23·97%, *syn*: 63·92% — according to GC/MS integrating on *m/e*=80; this sample was obtained via preparative GC (isothermal, 50 °C) of the triplet CHD dimers], 18 mg (0·088 mmol) of MDTBP, 20 mg (0·112 mmol) of phenanthrene (internal standard:IS) and 1·5 ml of DCM. The solution was cooled to 0 °C and then combined with *ca.* 30 mg ($2{\cdot}85 \times 10^{-2}$ mmol) of $(2,4\text{-}Br_2Ph)_3NSbCi_6$. The solution changed from a dark green (salt) to a dark amber in 5 sec. Another 30 mg portion of the aminium salt was added after 1 min accompanied by the same color change. After a total of 5 min., the reaction was quenched with methoxide (slight color change). The yield and product composition (%) were determined with GC/MS by integrating upon *m/e*=80(base peak) in the case of the CHD dimers and on *m/e*=178 (M^+ and base peak) for phenanthrene. The same column and GC parameters were used in all analyses.

	Diels–Alder		Cyclobutanes		All Dimers/IS	*Exo*/IS
	Endo	*Exo*	*Anti*	*Syn*		
Starting Material:	2·00	10·11	23·97	63·92	0·424	$7{\cdot}97 \times 10^{-3}$
Change:	+10·06	+25·68	−11·14	−24·6	—	—
Product:	12·06	35·79	12·83	39·32	0·218	$3{\cdot}0 \times 10^{-2}$

As indicated, the amount of *syn* lost closely matches the *exo* gained. The same holds true of the *anti*/*endo* pair. The GC/MS revealed that 51·4% of the original material remained.

The starting material was 87·89% cyclobutane while the product was 52·15% of the same. Assuming that all four isomers experienced decomposition equally, the change in cyclobutane composition, 35·74%, can be used to predict the product distribution according to a reaction path were retrocyclization of the cyclobutanes to monomer is followed by recyclization. Under aminium salt conditions, CHD is converted into a 4·56:1·0 *endo*/*exo* Diels–Alder isomer pair. Thus, the 35·74% loss of cyclobutanes is added to the already present amounts of Diels–Alder products observing the 4·56:1·0 *endo*/*exo* constraint (35·74=29·31+6·43 and 29·31/6·43=4·56). The results are below:

	Diels–Alder		Cyclobutanes	
	Endo	*Exo*	*Anti*	*Syn*
Starting Material:	2·00	10·11	23·97	63·92
Change:	+29·31	+6·43	−11·14	−24·6
Hypothetical Product:	31·31	16·54	12·83	39·32
Actual Product:	12·06	35·79	12·83	39·32

Clearly, the retrocyclization–dimerization sequence does not adequately predict the observed isomer distribution.

Rearrangement of pure *syn*-1,3-cyclohexadiene cyclobutane dimer with $(2,4\text{-}Br_2Ph)_3NSbCl_6$ in the presence of a hindered amine base

To a small vial charged with 10 mg ($6{\cdot}2 \times 10^{-2}$ mmol) of the *syn*-cyclobutane CHD dimer (93·1% isomerically pure according to GC/MS; prepared via triplet reaction of CHD and then isolated by preparative GC), 8 mg ($3{\cdot}7 \times 10^{-2}$ mmol) of MDTBP, 269 mg (1·51 mmol) of phenanthrene (IS), and 2 ml of DCM cooled to 0 °C was added (directly as the solid) two 35 mg ($3{\cdot}18 \times 10^{-2}$ mmol) portions of $(2,4\text{-}Br_2Ph)_3NSbCl_6$ with a 1 min interval between additions. After a total of 5 min, the reaction was quenched with sodium methoxide methanol. The results of GC/MS analysis are shown below:

	Diels–Alder		Cyclobutanes		All Dimers/IS	*Exo*/IS
	Endo	*Exo*	*Anti*	*Syn*		
Starting Material:	—	4·25	2·67	93·08	$4{\cdot}41 \times 10^{-2}$	$1{\cdot}81 \times 10^{-3}$
Product:	10·82	89·18	—	—	$9{\cdot}1 \times 10^{-3}$	$8{\cdot}12 \times 10^{-3}$

As the table reveals, 20·6% of the total material remained while the absolute amount of the *exo* isomer increased 4·48 fold. The lack of exact correspondence between the amount of *syn* lost and *exo* gained indicated a slight amount of retrocyclization/dimerization may have occurred either from the cyclobutanes, the Diels–Alder products, or both.

VCB rearrangement of *anti*-CB dimer of 1,3-cyclohexadiene

An enriched sample of the *anti*-CB dimer was rearranged in the same manner as for the *syn*. A sample which had the composition *endo*:*exo*:*anti*:*syn* = 0·74:5·78:83·79:9·70 (i.e. ~84% *anti*) was rearranged to afford a product of composition 49·61:8·58:41·01:0·81. The reaction is only *ca.* 50% complete, but the *endo*:*exo* ratio is 5·71:1 and if corrected for the percentages of *exo* and *endo* in the starting sample, the ratio is fully 17·4.

Reaction of *syn*- and *anti*-1,2-dimethyl-1,2-bis (2-methyl-1-propenyl) cyclobutanes with $(2,4\text{-}Br_2Ph)_3NSbCl_6$ in the presence of DTBP

To a 25 ml round bottomed flask was added 77 mg (0·401 mmol) of a 1·52:1·0 ratio (GC/MS) of the *anti* and *syn* head to head cyclobutane dimers of 2,4-dimethyl-1,3-pentadiene [41% (GC/TC) cyclobutanes and 59% 4-(2-methyl-1-propenyl)-1,3,3,4-tetramethylcyclohexene; this mixture was prepared by irradiation of a fluorenone saturated solution of neat 2,4-dimethyl-1,3-pentadiene for 2 days followed by chromatography (alumina, pentane) and distillation (2% yield)], 32 mg (0·17 mmol) of DTBP, 73 mg (0·41 mmol) of phenanthrene (IS), and 5 ml of DCM. After cooling to 0 °C and with stirring, 160 mg (0·196 mmol) of $(p\text{-}BrPh)_3NSbCl_6$ in 5 ml of DCM were added as rapidly as possible. After 8 min, the reaction was quenched with sodium methoxide/methanol, worked up with pentane/H_2O, filtered through cotton, and concentrated. Below are the results taken from GC/TC data:

	Cyclobutanes	Diels–Alder	DA/IS	All Dimers/IS
Starting Material:	41% *anti/syn* = 1·52	59%	0·527	0·824
Product:	23% *anti/syn* = 1·69	78%	0·60	0·781

GC/MS confirmed product identities as the same three dimers (no new peaks, same retention times) with $M^+=192$, $m/e=96(100\%)$ in each case.

Reaction of *syn*- and *anti*-1,2-dimethyl-1,2-bis(2-methyl-1-propenyl) cyclobutanes with $(p\text{BrPh})_3\text{NSbCl}_6$

To a small vial was added 46 mg (0·18 mmol) of a 3·86:10 *anti/syn* ratio (GC/FI) of the title cyclobutanes [30·5%, 69·5% was 4-(2-methyl-1-propenyl)-1,3,3,4-tetramethylcyclohexene as determined by GC/FI; for the preparation see the previous reaction], 28 mg (0·25 mmol) of cyclooctane (IS) and 5 ml of DCM. After cooling to −10°C, 10 mg ($1·2 \times 10^{-2}$ mmol) of $(p\text{-BrPh})_3\text{NSbCl}_6$ were added. After 10 min, the reaction was quenched with methoxide and analyzed by GC/FI:

	Cyclobutanes	Diels–Alder	DA/IS	All Dimers/IS
Starting Material:	30·5% *anti/syn* = 3·86	69·5%	0·684	0·984
Product:	19·6% *anti/syn* = 5·25	80·4%	0·81	1·01

As shown in the table, the yield was quantitative and the absolute amount of the Diels–Alder product increased by 18·4%. No 4-(2-methylpropenyl),3,3,5,5-pentamethylcyclohexene (the Diels–Alder dimer obtained from 2,4-dimethyl-1,3-pentadiene upon treatment with protic acid[29] or the aminium salt in the absence of base) was formed, as confirmed by GC/FI analysis of the product solution with and without the addition of authentic acid dimer.

The VCB rearrangement of (±)-(1*R*)-[4-methoxyphenyl]-(4*S*)-methyl-(2*S*)-vinylcyclobutane (the *anti* isomer of scheme 8)

This isomer was prepared as described previously.[28]

Photochemical run in the presence of base, a *trans*-anethole cation radical trap, and an internal standard

To a small vial was added 52 mg (0·26 mmol) of a 1·022/1·0 (GC/FI) mixture of the title compound and the corresponding Diels–Alder adduct (Scheme 8), 50 mg (0·390 mmol) of

DCB, 59 mg (0·29 mmol) MDTBP, 82 mg (1.0 mmol) of 2,3-dimethyl-1,3-butadiene (trap), 120 mg (0·112 mmol) of phenanthrene (IS), and 2 ml CH_3CN. Before irradiation, the following ratios were determined by GC analysis: (CB+DA)/standard=2·57, (DA+CB)/MDTBP=1·02, DA/standard=1·30, DA/MDTBP=0·515, DA/CB=1·022, and MDTBP/standard=2·52. After 10 min of irradiation, the following ratios were found: (CB+DA)/standard=2·284 (88·1% remained), (CB+DA)/MDTBP=0·909 (89·1% remained), DA/standard=2·01 (54% increase), DA/MDTBP=0·808 (57% increase), DA/CB=8·01, MDTBP/standard=2·491 (98·8% of original ratio). In addition, no *trans*-anethole, its dimer, nor cross adduct between *trans*-anethole and 2,3-dimethyl-1,3-butadiene were detected by GC/MS analysis. A control reaction in which DCB was omitted showed no change in starting materials after 10 min of irradiation [DA+CB:53 mg (0·26 mmol), MDTBP:53 mg (0·26 mmol), CH_3CN:2 ml].

Inhibition of the [1,3]-sigmatropic rearrangement by *trans*-anethole

To a small vial was added 25 mg (0·12 mmol) of the above DA+CB mixture (DA/CB=1·08 by GC), 14 mg (0·11 mmol) of DCB, 28 mg (0·14 mmol) of MDTBP, 22 mg (0·15 mmol) of *trans*-anethole, and 1 ml of CH_3CN. The table below shows the results obtained over 40 min of irradiation.

Time(min)	DA/MDTBP	CB/MDTBP	DA/CB	(CB + DA)/(MDTBP)	TA/MDTBP	TA-Dimer/MDTB
0	0·672	0·622	1·08	1·294	0·665	—
5	0·681	0·623	1·09	1·304	0·630	—
10	0·671	0·602	1·11	1·274	0·602	—
20	0·704	0·611	1·15	1·315	0·559	$1·68 \times 10^{-2}$
40	0·678	0·568	1·19	1·247	0·497	$2·94 \times 10^{-2}$

After this time, 50 mg (0·61 mmol) of 2,3,dimethyl-1,3-pentadiene were added. After an additional 10 min of irradiation, GC analysis showed the (*trans*-anethole + diene cycloadduct)/MDTBP = $1·56 \times 10^{-2}$.

Control reaction for reactivity: *trans*-anethole dimerization and cross addition to 2,3-dimethyl-1,3-butadiene

To a small vial was added 24 mg (0·16 mmol) of *trans*-anethole, 14 mg (0·11 mmol) of DCB, 28 mg (0·14 mmol) of MDTBP, and 2 ml of CH_3CH. The solution was irradiated for 10 min. Then, 45 mg (0·55 mmol) of 2,3-dimethyl-1,3-butadiene were added and the resulting mixture was irradiated for an additional 30 min. The results of GC analysis are recorded below:

Time(min)	TA/MDTBP	TA-Dimers/MDTBP	Cross adduct/MDTBP
0	0·705	0	—
10	0·643	$8·32 \times 10^{-3}$	—
	2,3-dimethyl-1,3-butadiene added		
10	0·598	$1·13 \times 10^{-2}$	0·166
20	0·510	$1·712 \times 10^{-2}$	0·207

[1,3]-Sigmatropic rearrangement with 10·3 mol % $(4\text{-BrPh})_3NSbCl_6$ for 3 min

In the usual manner, 52 mg (0·25 mmol) of the DA+CB mixture (DA/CB=1·22 by GC) was reacted with 26 mg (0·03 mmol, 10·34 mol%) of $(p\text{-BrPh})_3NSbCl_6$ in 3 ml of DCM at 0 °C in the presence of 18 mg (0·1 mmol) of phenanthrene (internal standard). After 3 min, the reaction was stopped with methoxide and analyzed by GC; the results are below.

Time(min)	(CB + DA)/standard	DA/standard	DA/CB
0	2·75	1·51	1·217
3	2·15	1·9	7·7

Hence, the total DA content increased 25·8% while the total recovery of material was 78·2%.

[1,3]-Sigmatropic rearrangement with 7·4 mol % of $(4\text{-BrPh})_3NSbCl_6$ for 90s

To a 10 ml round bottomed flask equipped with a stir bar was added 47 mg (0·23 mmol) of CB+DA (DA/CB=1·11 by GC/FI), 19 mg (0·11 mmol) of phenanthrene (internal standard), and 2 ml DCM. After cooling to 0 °C, 14 mg (0·017 mmol, 7·4 mol%) of $p\text{-BrPh})_3NSbCl_6$ were added all at once. After 90s, the reaction was quenched with methoxide. The results are shown below:

Time(min)	(DA + C)/standard	DA/standard	DA/CB
0	2·205	1·16	1·11
1·5	2·22	1·51	2·11

Hence, the DA adduct increased by 30·2% while recovery of material was essentially quantitative within experimental error.

Preparation and rearrangement of (±)-(1*R*)-(4-methoxyphenyl)-(4*S*)-methyl-(2*R*)-vinylcyclobutane (the *syn* isomer of scheme 8)

Into an immersion photochemical reaction vessel was placed *ca.* 20 ml of 1,3-butadiene and 1·3 g (8·8 mmol) of TA. The stirred solution was irradiated for 6 hours at −35 °C. After the butadiene had been allowed to evaporate, the crude mixture was taken up in pentane and analyzed by GC/MS. Detected were *cis*- and *trans*-anethole, six apparent cross adducts [M^+=202, *m/e*=148(100%)], and an apparent anethole dimer [M^+=256, *m/e*=147(100%)]. GC/FI showed only 4 major cross adduct peaks eluting in 2 groups of 2. The 4 adducts were believed to be 2 vinylcyclobutanes and 2 Diels–Alder adducts formed from both *cis*- and *trans*-anethole (see below):

Crude Product Composition (GC/FI)%

Cis- and *Trans*-Anethole	CB1	CB2	DA1	DA2	Anethole Dimer
21	3	22	2	21	31

Thick layer chromatography (pentane/benzene:5/1) separated the material into a major and minor band; the major band contained primarily CB2 and DA2 while the minor band consisted mostly of CB1 and DA1. DA2 was identified as the known Diels–Alder adduct[28] derived from *trans*-anethole (under cation radical conditions) by GC analysis of the major band spiked with the authentic adduct. However, CB2 did not correspond with the known cyclobutane[28] formed from *trans*-anethole under cation radical conditions although it was later rearranged (see below) into DA2 under PET conditions. Rerunning the major band on a thick layer plate (pentane/benzene:5/1) eventually lead to the isolation of CB2 as a 6·83:1·0 mixture with the known cyclobutane adduct formed from *trans*-anethole under cation radical conditions being the minor component.

In the ^{1}H-NMR spectrum of the purified material (which, incidentally, had the same peaks, multiplicities, integrations, but slightly different chemical shifts when compared with the ^{1}H-NMR[28] of the *anti*-isomer), the benzylic proton absorption was identical in shape but downfield from the analogous absorption in the spectrum of the cation radical cyclobutane adduct. This behavior can be rationalized by invoking a shielding effect from the induced magnetic field of the double bond upon the benzylic proton in the *anti*-cyclobutane where the ethenyl groups and the benzylic proton are presumed to be *syn*. In CB2, where the ethenyl group and the benzylic proton are presumed to have an *anti* relationship, no shielding should occur and a relatively downfield chemical shift for the benzylic proton absorption is reasonable. ^{1}H-NMR ($CDCl_3$, 500MHz)δ 1·18 (d, 3H, J=6·83, ring methyl), 1·83–1·91 (m, 1H, methylene proton), 2·01 (dt, 1H, J=7·88 and 3·68, methylene proton), 2·76 (septet, 1H, J=7·88, methine adjacent to methyl), 3·18 (quartet, 1H, J=7·88, allylic methine), 3·24 (t, 1H, J=9·46, benzylic proton), 3·79 (s, 3H, methoxy methyl), 4·88–4·96 (m, 2H, J=10·51 and 18·4, terminal vinyl protons), 5·67–5·74 (m, 1H, vinyl proton next to ring), 6·81–7·06 (m, 4H, aromatic). ^{13}C-NMR ($CDCl_3$, 500MHz)δ a) 20·8, b) 31·8, c) 32·9, 3) 41·2, 3) 50·4, f) 55·5, g) 113·5, h) 114·1, i) 128·6, j) 133·8, k) 139·9, l) 157·8.

Rearrangement

A small flask containing 50 mg (0·25mmol) of the above *syn* isomer (6·83:1·0 mixture of CB2 and the cation radical (*anti*) cyclobutane adduct), 7mg (0·05 mmol) of DCB and 0·25 ml of CH_3CN was irradiated for 30 min. GC showed that conversion was essentially complete (DA2/CB2=11·4). The identity of DA2 was confirmed by GC analysis of the product solution spiked with authentic DA2.

Reaction of *trans*-anethole with *E,E*-2,4-hexadiene by direct irradiation: formation of (±)-(1*R*)-(4-methoxyphenyl)-(2*S*)-(1-*E*-propenyl)-(3*R*, 4*S*)-dimethylcyclobutane (*syn* isomer of scheme 9)

To a medium size pyrex vial was added 1·0 g (6·7 mmol) of TA and 6·73 g (82 mmol) of *E,E*-2,4-hexadiene. After the sample had been irradiated for 2 days, another 1·0 g (6·7 mmol) of TA was added (piecemeal addition was used to minimize TA dimerization). After 3 days additional irradiation (most of the TA had been consumed by GC), the sample was concentrated. GC revealed a TA dimer/cross product (see below) ratio of 4:1. The crude material was chromatographed on 100 g of silica gel with 5:1 Skelly B/benzene. GC analysis of the combined 5th–60th 10ml fractions showed *cis*- and *trans*-anethole plus the cross adducts. Distillation at 1mm gave three fractions: 1) 60 °C–90 °C: *cis*- and *trans*-anethole, 2)

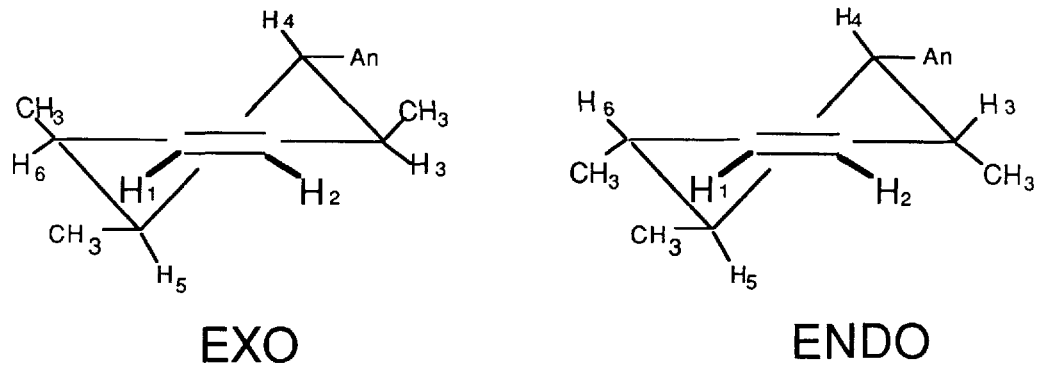
90°C–110°C: anetholes + cross adduct (*ca.* 1:1), and 3) 110°C–120°C: anetholes + crossadducts (1:3). The 3rd fraction was chromatographed on a thick layer plate using 9:1 pentane/ether. The product band was cut into thirds: 1) the top third was cross adduct plus a trace of anetholes by GC, 2) the 2nd third contained significant amounts of anetholes, and 3) the last cut contained unidentified materials plus cross adduct. The 2nd third was heated at 60°C at 1 torr for 12h (removal of the anetholes) rechromatographed (thick layer, 9:1 pentane/ether) and combined with the first third. The total amount of cross adduct recovered was 100 mg (3·2%).

GC/MS showed 11 isomers with one comprising 66% of the total. The remaining isomers were present in 1%–9% abundance each. For the major isomer, the mass spectrum showed *m/e*=174 as the largest ion and a base peak of 148. The *m/e*= 174 ion probably arises from the loss of 2-butene (C_4H_8) from the parent ion of a cyclobutane adduct (see below): 230 − 56 = 174. This behavior is precedented by other TA/cyclobutane adducts. One isomer (0·85%), which showed M^+=230 and *m/e*=148 (100%), serves as a stark contrast insofar as the stability of its parent ion is concerned. The major isomer corresponded with one of the initially formed non-Diels–Alder isomers in the reaction of TA with *E,E*-2,4-hexadiene under aminium salt conditions at −30°C after 55s. The ^{1}H-NMR spectrum was consistent with a vinylcyclobutane cross adduct. The benzylic proton absorption appeared at δ 3·2 as a symmetrical triplet without any hint of additional fine coupling (500 MHz). The chemical shift is downfield from that for the analogous proton (δ 2·7) in the cyclobutane formed from TA 1,3-butadiene under aminium salt (cation radical) conditions but the same as for the analogous proton in the cyclobutyl adduct formed from TA and 1,3-butadiene by direct, unsensitized irradiation. It is clear the benzylic proton should experience shielding when it is *syn* to an alkenyl group—as in the *trans/anti/trans* isomer—more than when in an *anti* relationship with the same, as in the *trans/syn/trans* isomer. Hence, the cyclobutanes formed from direct irradiation are predicted to have the *trans/syn/trans* relationship. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 1·08 (t, 6H, *J*=6·3, two methyl groups on the ring. This peak is actually two doublets superimposed; in the 90 MHz spectrum a lone doublet appears.), 1·51 (d, 3H, *J*=5·8,. allylic methyl), 2·28 (hex, 1H, *J*=6·3, methine H on ring carbon diagonal to the carbon bearing the anisyl group), 2·65–2·75 (m, 2H, allylic methine and methine on diagonal carbon: the COSY spectrum indicated this absorption was coupled with a vinyl proton and a ring methyl group), 3·21 (t, 1H, *J*=6·3, benzylic methine: the COSY experiment showed coupling only to the area at δ 2·65–2·75), 3·78 (s, 3H, methoxy methyl), 5·15–5·21 (dd, 1H, *J*=8·9 and 15·8, vinyl proton adjacent to ring: COSY shows coupling to allylic methine in ring), 5·27–5·34 (quartet, 1H, *J*=5·8 and 15·8, vinyl H adjacent to allylic methyl), 6·82 (d, 2H, *J*=10·0, aromatic), 7·05 (d, 1H, *J*=10·0, aromatic). ^{13}C-NMR ($CDCl_3$, 500 MHz) δ a) 14·56. b) 15·03, c) 17·9, d) 34·20, e) 35·45, f) 47·89, g) 47·94, h) 55·16, i) 113·34, j) 124·68, k) 128·88, l) 132·33, m) 134·20, n) 157·56. HRMS: *m/e* calculated ($C_{12}H_{22}O$): 230·167055, *m/e* found: 230·16640.

VCB rearrangement of (±)-(1R)(4-methoxyphenyl)-(2*S*)-(1-*E*-propenyl)-(3*R*, 4*S*)-dimethylcyclobutane

To a small vial was added 70 mg (0·304 mmol) of 66% title cyclobutane (see the previous experimental), 44 mg (0·34 mmol) of DCB, 61 mg (0·32 mmol) of DTBP, and 1·5 ml of CH_3CN. After 92 min of irradiation, the reaction mixture was concentrated, taken up in pentane (DCB precipitated), and chromatographed (thick layer, 5:1 pentane/benzene) affording 57 mg of crude product which was still *ca.* 22% (by GC) *cis*- and *trans*-anethole. Hence, the material was heated at 55°C for 6h at 1torr. After additional chromatography

(thick layer, 5:1, pentane/benzene), GC analysis showed only a trace of the anetholes. There were 3 major components in the mixture according to GC/FI in a 6·13:1·0:1·59 ratio. The identities of the products were the two known Diels–Alder adducts and a presumed cyclobutane (not starting material) respectively (established via GC/MS analysis of the reaction after 15 min of irradiation spiked with authentic Diels–Alder adducts). A total of 39 mg were recovered 82% of which were Diels–Alder products or 70·3% of which was the *exo* isomer (see NMR analysis below). Hence, a 59·3% yield of the *exo* isomer based on the starting cyclobutane was obtained.



Scheme 14

The ^{1}H-NMR of a near 1:1 mixture of the known Diels–Alder adducts[28] had absorptions which exactly matched the peaks seen for the major product of the rearrangement reaction; three upfield methyl doublets, methoxy singlet, exact olefinic and aromatic chemical shifts and splitting patterns were among the more obvious matches. The spectrum of the present reaction product showed clear differences relative to the starting cyclobutane excluding the possibility of an isomerization (rather than rearrangement) reaction. The olefinic region of the 500 MHz ^{1}H-NMR product spectrum showed 8 equally spaced lines for one proton and a doublet of triplets for another. Examination of structures of the *exo* and *endo* Diels–Alder adducts shows that such splitting is reasonable for both isomers. In the *exo* isomer, H_1 is coupled with pseudoequatorial H_6 (dihedral angle $<<90°$) and vinylic H_2 due to proximity and pseudoaxial H_3 since allylic coupling is best when the dihedral angle approaches 90°. A reasonable order for the magnitudes of the coupling constants would be $J_{H_1-H_2} > J_{H_1-H_6} > J_{H_1-H_3}$. The 8 observed lines are each separated by 2·63 Hz, a value consistent with substantial allylic coupling ($J_{H_1-H_3}$). Doubling this value gives 5·27 Hz — a reasonable value for $J_{H_1-H_6}$ according to the Karplus equation ($J=8{\cdot}5\cos^2\phi - 0{\cdot}28$, $0° \leq \phi \leq 90°$) if the dihedral angle lies between 31° ($J=6$ Hz) and 38° ($J=5$ Hz) which is probable. Doubling again gives 10·51 Hz — a reasonable J for *cis* vinylic coupling ($J_{H_1-H_2}$). Hence a doublet of doublet of doublets, or 8 equally spaced lines, is a reasonable splitting pattern for H_1. In contrast, H_2 would probably be coupled significantly only to H_1 since the H_2—H_3 and H_2—H_6 dihedral angles are *ca.* 90° and $<<90°$ respectively. These latter two couplings though slight might be detectable; hence, for H_2, a basic doublet with each line split into a small triplet is consistent. A similar analysis of the *endo* isomer leads to the overall same conclusions: H_1 could be expected to couple strongly with H_2 but weakly to H_6 and H_3 resulting in a doublet of triplets while H_2 could be significantly coupled to H_1, H_6, and H_3 leading to a doublet of doublet of doublets.

Differentiation between the *endo* and *exo* isomers can perhaps be facilitated by the respective splittings for H_4. In the *endo* isomer, H_4 is in a *gauche* relationship with H_3 but an *anti* relationship with H_5; the H_4—H_3 and H_4—H_5 couplings should differ and a doublet of doublets is predicted. However, in the *exo* isomer, the H_4—H_3 and H_4—H_5 relationships are both *anti* and a triplet is indicated. In the ^{1}H-NMR spectrum of both isomers (*exo*/*endo*=1·4), a clear doublet of doublets (J=5·26 and 11·04) is observed at δ 2·71. The chemical shift and J values are consistent with the benzylic methine of the *endo* isomer. However, in the product of the rearrangement this absorption is absent. A 2 dimensional (standard) C—H correlation experiment performed on the rearrangement product showed that the proton represented by the upfield portion of a multiplet at δ 1·98–2·11 in the ^{1}H-NMR spectrum was coupled to a carbon at δ 49 in the ^{13} C-NMR which most likely bears the anisyl moeity (of the sp^3 carbons, only the methoxy methyl was farther downfield at δ 55). This portion of the multiplet has 4 lines which appear as a doublet of doublets with J values of 9·99 Hz and 11·04 Hz — a near triplet. A COSY (^{1}H-NMR) experiment showed that this near triplet is not coupled to any of the methyl groups (upfield doublets). In addition, the coupled ^{13}C-NMR spectrum showed the correlated carbon as the expected doublet. Hence the *exo* structure is suggested.

The *endo* isomer's ^{1}H-NMR assignments can be made from the spectrum of the 1·4:1·0 *exo*/*endo* mixture since the *exo* signals have been distinguished as described above. The *endo* and *exo* adduct structure assignments are both strongly supported by a comparison with the *endo*- and *exo*-DA adducts of *E,E*-2,4-hexadiene with acrylonitrile.[40]

Exo isomer

^{1}H-NMR ($CDCl_3$) δ 0·57 (d, 3H, J=6·31, methyl on C_3), 0·78 (d, 3H, methyl on C_5), 0·92 (d, 3H, J=6·61, methyl on C_6), 2·01 (dd, 1H, J=9·99 and 11·04, benzylic methine-H_4), 2·03–2·11 (m, 2H, complex, allylic methine-H_3), 2·2–2·31 (m, 2H, complex, H_5 and H_6), 3·79 (s, 3H, methoxy methyl), 5·52 (dt, 1H, J=9·46 and 0·52, vinyl H_2), 5·45 (ddd, 1H, J=2·63, 5·27, and 10·51, vinyl H_1), 6·82 (d, 2H, J=8·41, aromatic H *meta* to methoxy), 7·04 (d, 2H, J=8·41, aromatic H *ortho* to the methoxy). The ^{13}C-NMR spectrum was assigned from a C—H correlation experiment and a coupled ^{13}C-NMR spectrum: ^{13}C-NMR ($CDCl_3$) δ a) 15·30, b) 17·34, c) 20·27, d) 35·25, e) 36·65, f) 39·17, g) 49·09, h) 55·17, i) 113·52, j) 129·16, k) 131·91, l) 132·59, m) 136·93, n) 157·74.

Endo isomer

^{1}H-NMR ($CDCl_3$) δ 0·72 (d, 3H, J=6·31, allylic methyl closest to anisyl group), 0·82 (d, 3H, J=6·31, non-allylic methyl), 1·09 (d, 3H, J=6·31, allylic methyl farthest from the anisyl group), 1·68 (dhex, 1H, J=5·78 and 9·46, H_5), 1·89 (pentet of t, 1H, J=5·3 and 10·25, H_6), 2·19 (sextet of d, 1H, J=7·88 and 0·53, H_3), 2·71 (dd, 1H, J=5·26 and 11·04, H_4), 3·79 (s, 3H, methoxy methyl), 5·45 (dt, 1H, J=10·5 and 1·05, H_1), 5·22 (ddd, 1H, J=2·63, 5·27, and 10·51, H_2-splitting assigned by analogy with the *exo* isomer), 6·8–7·07 (m, 4H, aromatic). ^{13}C-NMR ($CDCl_3$) δ a) 16·89, b) 18·32, c) 20·69, d) 33·25, e) 36·39, f) 39·52, g) 50·56, h) 55·05, i) 113·29, j) 130·15, k) 131·74, l) 132·42, m) 135·57, n) 157·72 (assigned via C—H correlation experiment).

VCB rearrangement of (±)-(1*R*)-(4-methoxyphenyl)-2*S*-(1-*E*-propenyl)-(3*R*, 4*S*)-dimethylcyclobutane under PET conditions in the presence of MDTBP and *trans*-1,3-Pentadiene

To a small vial was added 25 mg (0·11 mmol) of the title cyclobutane (73%; 8 significant signals 7 of which represented 27%: as determined by capillary GC/FI; most were 3–4%, the smallest major isomer/minor isomer ratio was 8·34:1; only a trace of *cis/trans* anetholes were detected), 16 mg (0·13 mmol); of DCB, 35 mg (0·51 mmol) of *trans*-1,3-pentadiene (trap), 20 mg (0·097 mmol) of MDTBP, 18 mg (0·1 mmol) of phenanthrene (internal standard), and 1 ml of CH_3CN. The results from GC/FI are tabulated below.

Time	CB/IS	DA_{maj}/IS	DA_{maj}/DA_{min}	CB+DA_{maj}/IS	DA_{maj}/CB	TA-PD adduct/IS
0	0·884	—	—	0·884	—	—
15 min	0·373	0·609	7·92	0·98	1·63	trace
30 min	not integrated	0·974	6·80	1·10	6·5	0·19
54 min	traces	1·03	6·82	1·03	CB not detected	0·295

[Abbreviations: CB=major cyclobutane; IS=internal standard (phenanthrene); DA_{maj}=major Diels–Alder (*exo*); DA_{min}-minor Diels–Alder (*endo*); TA-PD adduct=*trans*-anethole/1,3-pentadiene Diels–Alder adduct]

The identities of the Diels–Alder products were established by spiking the reaction mixture after 15 min irradiation with authentic adducts and subsequent GC/FI and GC/MS analysis. The *trans*-anethole/1,3-pentadiene adduct[28] was characterized by GC/MS where a peak with M^+=216 and *m/e*=148 (100%) was found.

VCB rearrangement of (±)-(1*R*)-(4-methoxyphenyl)-(2*S*)-(1-*E*-propenyl)-(3*R*, 4*S*)-dimethylcyclobutane under PET conditions in the presence of *cis* and *trans* anethole

To a small pyrex vial was added 52 mg of a 2·51:1·0 title cyclobutane/anethole mixture (7 other cross adducts were also present with only one being present in a significant quantity – major cyclobutane/second most plentiful isomer = 6·3 as determined by GC/FI), 27 mg (0·211 mmol) of DCB, and 1 ml of CH_3CN. Before irradiation, GC/MS revealed none of the *exo* Diels–Alder product. After 20 min and again after 40 min of irradiation, GC/MS showed small amounts of the *exo* isomer with virtually no other concurrent changes in the other isomers present. Hence, the only impact the presence of the anetholes had was rate reduction. The identity of the *exo* isomer was established by spiking the 40 min reaction mixture with a known sample and subsequent GC/MS analysis. After 24 h of irradiation, the reaction was essentially complete (*exo* isomer/cyclobutane >15).

Preparation of phenyl propenyl sulfide (PhPrS)

This sulfide was prepared from phenyl vinyl sulfide (PVS) according to a literature[41] procedure in a 3·84:1·0 product/PVS ratio (2nd fraction: 64–70 °C, 10 torr). Product identity verified by ^{1}H-NMR.

Reaction under PET conditions for 48 h.

To a pyrex test tube was added 674 mg (79·3%, 535 mg–3·56 mmol) of PhPrS (M^+=150, base peak=59), 408 mg (3·04 mmol) of DCP, 350 mg (2·73 mmol) of DCB, and 11 ml of CH_3CN. After 48 h of irradiation, the crude mixture was concentrated, diluted with pentane, filtered from solids and concentrated, purified from unreacted starting materials by evaporation *in vacuo* (1 torr) for 3 h, and chromatographed (thick layer, Skelly B), affording 202 mg (0·71 mmol, 23·4%) of a 3·63:1·0 (GC/FI) mixture of isomers as a clear and colorless oil. Each isomer had a M^+=284 and a base peak of *m/e*=175 (M^+=109) according to GC/MS analysis. The ^{1}H-NMR spectrum had no olefinic absorptions and the correct integration for a Diels–Alder cycloadduct. The ^{13}C-NMR spectrum had 11 lines with chemical shifts < 60 Hz — a fact also consistent with a cycloadduct structure. The NMR and mass spectral behavior are consistent with a Diels–Alder adduct. ^{1}H-NMR (CS_2, 90 MHz) δ (major isomer) 1·1 (s, 3H methyl), 1·3–3·0 (m, 16H, ring protons), 6·7–7·2 (m, 5H, aromatic). ^{13}C-NMR ($CDCl_3$, 80 MHz) δ a) 21·98, b) 23·29, c) 26·82, d) 27·90, e) 29·35, f) 32·85, g) 35·69, h) 36·32, i) 39·50, j) 49·24, k) 51·44, l) 128·38, m) 131·14, n) 132·28, o) 134·94, p) 137·42, q) 137·91. HRMS: *m/e* calculated for $C_{19}H_{24}S$:284·15987; measured 284·16085.

Reaction with $(4\text{-BrPh})_3NSbCl_6$ in the presence of base

To a 25 ml round bottom flask was added 160 mg (1·19 mmol) of DCP, 224 mg (79·3%, 194 mg–1·29 mmol) of PhPrS, 186 mg (0·91 mmol) of MDTBP and 5 ml of DCM. After cooling to 0° C and while stirring, 494 mg (0·615 mmol) of $(4\text{-BrPh})_3NSbCl_6$ in 10 ml of DCM was added as rapidly as possible. After 5 min, the reaction was quenched with methoxide and analyzed. GC/MS revealed one small product peak which had M^+=284 and a base peak of 175. Also prominent was *m/e*=134 (75%). This is in contrast to the adducts obtained under PET conditions (see above) where *m/e*=134 was only 10% of the base peak. GC/MS analysis of the crude reaction product combined with the PET adducts showed that the different reactions gave different products. Also detected were one DCP dimer [M^+=268, *m/e*=134(100%)], a DCP/PVS cross adduct (M^+=270, *m/e*=134 (100%)], and an unknown material [largest *m/e*=base peak=134].

Reaction under PET conditions for 4 h

To a small pyrex vial was added 69 mg (0·51 mmol) of DCP, 106 mg (79·3%, 84·1 mg–0·56 mmol) of PhPrS, 67 mg (0·523 mmol) of DCB and 2 ml of CH_3CN. After 4 h of irradiation, GC/MS revealed 4 apparent cross adduct peaks, two of which were demonstrated to be the Diels–Alder adducts formed after 48 h or irradiation by GC/MS analysis of the product solution spiked with the known adducts (see above). The larger of the remaining 2 products (the major product of the reaction) had exactly the same retention time and mass spectrum as the cross adduct formed under aminium salt conditions (see above). The remaining adduct — seen only in this experiment — had a M^+=284, *m/e*=175 (100%), and 134 (33%). These latter 2 products are speculated to have the cyclobutane cross adduct structure based upon their mass spectral behavior and the process of elimination. Also detected was PVS dimer [largest *m/e*=244=272−28 (M^+-ethylene), *m/e*=135 (100%)], a DCP/PVS cycloadduct [M^+=270, *m/e*=134 (100%)], and a PVS/PhPrS cross adduct [M^+=286, *m/e*=150 (100%), 135 (61%), 136 (57%)]. A control reaction where DCB was omitted and the sample was irradiated for 16·5 h produced only traces (<<1%) of one peak which contained *m/e*=175 in its mass spectrum: largest *m/e*=175 (93%), *m/e*=135 (100%).

VCB rearrangement of (±)-(*S*)-3-methyl-(*R*)-1-phenylthio-(*S*)-2-[1-E-propenyl] cyclobutane the *anti* isomer of scheme 11 under PET conditions.

The title cyclobutane was prepared under PET conditions in 35% yield upon purification with thick layer (Skelly B) chromatography. The following physical data established the structure of the *anti*-CB starting material: ^{1}H-NMR (200 MHz) δ 7·6–7·4 (m, 5H), 5·5 (m, 2H), 3·35 (q, 1H, *J*=9·0 H z, 2·5–1·5 (m, 4H), 1·65 (d, 3H, *J*=5 Hz), 1·05 (d, 3H, *J*=6H); ^{13}C-NMR (80 M Hz) δ a) 17·88, b) 20·15, c) 34·38, d) 36·63, e) 43·48, f) 54·50, g) 125·78, h)126·09; i) 128·65, j) 130·23, k) 130·48, l) 132·20. The small amount of *syn* isomer present differed primarily in the chemical shift of methine proton alpha to the phenylthio function which was shifted downfield to δ 3·75 (from 3·35 in the *anti* isomer) and appears as a clean quartet (*J*=8·0 Hz). Both the upfield shift of the major isomer and its splitting pattern (two diaxial and one ae splitting) clearly distinguish it as the *anti* isomer. HRMS: *m/e* calculated: 218·11292, *m/e* measured 218·11209.

To a small vial was added 30 mg (0·14 mmol) of the title compound [obtained from the PET cycloaddition of *E,E*-2,4-hexadiene and PVS for 24h] as a 2·18 *anti/syn* mixture (19·6:1 ratio of CB:DA adducts): 4 mg of DCB, and 2 ml of dry acetonitrile. n-Decane was employed as the internal standard. The reaction mixture was irradiated for a total of 20 h, with GC monitoring at various time intervals. The results are summarized below:

Time(Hr)	CB/DA	(CB+DA)IS	% Conv.	% Decomp.
0	19·61	4·37	0	0
2	19·16	5·08	5·2	0
5	1·97	4·72	26·0	0
20	0·25	3·91	78·0	11

After the usual PET workup procedure, the crude product was chromatographed on silica gel (hexane).

The VCB rearrangement product

^{1}H-NMR (200 MHz) δ 7·15–7·45 (m, 5H), 5·65 (ddd, 1H, *J*=12·5, 5·0, 2·6 Hz), 5·52 [d(br), 1H, *J*=12·5], 3·55 (ddd, 1H, *J*=9·9, 5·0, 2·7 Hz), 2·5–1·2 (m, 4H), 1·05 (d, 3H, 6·5 Hz), 0·96 (d, 3H, 6·5 Hz); HRMS: *m/e* calculated: 218·11292, *m/e* 218·11209 measured. The multiplicities and coupling constants of the vinyl protons and the proton alpha to the phenylthio function are highly characteristic of an *endo*-DA isomer, as has clearly been established in the case of the *endo*- and *exo-E,E*-2,4-hexadiene/acrylonitrile adducts.[40] The ratio of *endo* to *exo* DA product is 3:1. The alpha proton of the latter has δ 3·16 (ddd, *J*=3·5, 5·7, 7·5 Hz).

Cycloaddition of 1,1′-dicyclopentenyl and phenyl vinyl ether

A solution of 1,1′-Dicyclopentenyl[41](4·0 g, 0·029 mol) and phenyl vinyl ether (8·7 g, 0·0725 mol) in freshly distilled dry acetonitrile (29·0 ml) containing 1,4-dicyanobenzene (0·74 g, 0·0058 mol) was photolyzed for 42 h. The solvent was removed by rotary evaporation and the

crude product purified by chromatography on silica gel (hexane) to afford 1·51 g (20% yield) of CB and DA adducts. The first pair of adducts (GC/MS) is the *syn*:*anti* CB pair (7:1), and the second pair corresponds to the Diels–Alder adducts (2:1). The ratio of CB:DA adducts aggregatily is 2·89:1. The CB adducts were characterized as follows: Mass spectrum *m/e* 254 (M^+, 1%), 161 (30%), 134 (100%), 119 (15%), 105 (18%), 93 (25%), 91 (42%), 77 (20%), 67 (15%), and 41 (21%). The retrofragmentation reaction and the presence of a weak molecular ion chracterize both adducts as cyclobutane adducts; ^{1}H-NMR (300 MHz $CDCl_3$) δ 7·35–7·15 (m, 2H), 7·00–6·70 (m, 3H), 5·55–5·45 (brt, 1H), 4·43 (t, *syn*, 1H, *J*=6·3 Hz), 3·90 (t, *anti*, 1H, *J*=5·70 Hz), 2·84–1·40 (brm, 15 H); HRMS: Calculated for $C_{18}H_{22}O$, 254·16707; measured, 254·16628; ^{13}C-NMR($CDCl_3$) *syn* isomer: a) 157·0, b) 145·0, c) 128·3, d) 123·2, e) 119·5, f) 114·5, g) 76·4, h) 36·6, i) 36·3, j) 31·8, k) 31·4, l) 31·2, m) 30·2, n) 24·8, o) 23·3.

Rearrangement of the CB cycloadducts derived from 1,1′-dicyclopentenyl and PVE

The title CB adducts (18 mg, 0·0709 mmol) were dissolved in 1·0 ml dry dichloromethane and the solution cooled to −45 °C (aqueous $CaCl_2$/dry ice) under an atmosphere of dry nitrogen. Tris (2,4-dibromophenyl) aminium hexachloroantimonate (20 mg, 0·0195 mmol) was added in small portions over 15 min. After 27 min, the reaction was quenched with sodium methoxide/methanol solution. The crude mixture was extracted with ether (3×10 ml) and the united extracts washed with water and dried over magnesium sulfate. Chromatography on silica gel (hexane) afforded the rearranged Diels–Alder adducts (9·0 mg, 50%). Capillary GC studies revealed a pair of DA adducts (2:1, *exo*:*endo*):

Time(min)	CB+DA/ref	CB/ref	DA/ref	CB/DA
0	0·494	0·330	0·159	2·07
14	0·414	0·121	0·293	0·41
27	0·39	0	0·385	0

The kinetic data above reveal that complete conversion of the CB adducts occurs, corresponding to a 67% yield of DA adducts. Mass spectrum: M^+=254 (8%), 161 (100%), 134 (62%), 119 (20%), 105 (20%), 91 (47%), 79 (35%), 67 (34%), 41 (28%); ^{1}H-NMR (360 MHz, $CDCl_3$): δ 7·30–7·10 (m, 2H), 7·0–6·85 (m, 3H), 4·70 (dt, 1H, *J*=10·2(d), 4·7 (t) Hz, *endo*), 4·27 (q1H, *J*=5·15 Hz, *exo*), 2·85–1·40 (brm, 16H); HRMS: Calculated for $C_{18}H_{22}O$: 254·16707; measured 254·16652.

Rearrangement of *syn* and *anti* 1-methyl-3-phenylthio-2(1-propenyl)cyclobutanes under PET conditions in the presence of MVA (trap study)

The title cyclobutane was prepared from a 16·7h PET reaction of 874 mg (6·42 mmol) of PVS, 1·586 g (19·31 mmol) of *E,E*-2,4-hexadiene, and 762 mg (5·95 mmol) of DCB in 15 ml of CH_3CN. A 28·9% yield (404 mg, 1·85 mmol) of cyclobutanes was obtained upon purification of the crude product by : 1) evaporation of CH_3CN, 2) precipitation of polymeric impurities with pentane, and 3) column chromatography (100 g silica gel, Skelly B; Rf=0·1). To a small pyrex vial was added 26 mg (0·12 mmol) of the title cyclobutanes (*anti*/*syn*=3·06; Σ

cyclobutanes/decane=1·13; Diels–Alder(*endo* adduct)/decane=0·061), 42 mg (0·424 mmol) of MVA (trap: MVA/decane=1·6), 4 mg (0·0031 mmol) of DCB, 17 mg (0·12 mmol) of decane, and 2 ml of CH_3CN. After 3h of photolysis, the following ratios were obtained from electronic integration: Σ cyclobutanes/decane=0·531, Diels–Alder/decane=0·105 (72% increase), MVA/decane=1·035. After 6h of photolysis, the following ratios were obtained: Σ cyclobutanes/decane=0·458, Diels–Alder/decane=0·132 (116% increase from the beginning, and MVA/decane=0·856. After 9h photolysis, the *exo* Diels–Alder adduct was detected. Despite this, the Σ Diels–Alder/decane ratio decreased slightly to 0·111. The other ratios determined were Σ cyclobutanes/decane=0·260 and MVA/decane=0·636. GC/MS analysis was employed for product identification. *None* of the known MVA/*E,E*-2,4-hexadiene cyclobutane cross product nor any PVS/MVA adducts were detected via GC/MS. A control reaction to demonstrate the viability of formation of the various possible cycloadducts derivable from PVS, MVA, and *E,E*-2,4-hexadiene while simultaneously present in the same reaction was then performed. To a small pyrex vial was added 73 mg (0·54 mmol) of PVS, 51 mg (0·52 mmol) of MVA, 43 mg (0·52 mmol) of *E,E*-2,4-hexadiene, 22 mg (0·17 mmol) of DCB, 72 mg (0·52 mmol) of *n*-decane (internal standard), and 2 ml of CH_3CN. All products were identified by GC/MS and quantified via GC/FI. After 4h of photolysis, the following ratios of products were obtained: (Σ PVS/hexadiene cycloadducts)/decane=0·105, (Σ PVS/MVA cycloadducts)/decane=0·116, (Σ MVA/hexadiene cycloadducts)/decane=0·014. After 7h the following ratios were determined: (Σ PVS/hexadiene cycloadducts)/decane=0·088, (Σ PVS/MVA cycloadducts)/decane= 0·061, (Σ MVA/hexadiene cycloadducts)/decane=0·0046. The PVS/MVA adduct [M^+=235, *m/e*=136(100%), *m/e*=99(7%). *m/e* =57(27%)] was not fully characterized but nevertheless showed mass fragmentation behaviour typically associated with the cyclobutanes produced via cation radicals in this laboratory. Hence MVA is demonstrated to be an appropriate trap for this rearrangement.

Rearrangement of *syn* and *anti* 1-methyl-3-phenylthio-2(1-propenyl)cyclobutanes under PET conditions in the presence of 1-ethenyl-4-(2-propenyl)cyclohexene(trap study).

To a small pyrex vial was added 26 mg (0·12 mmol) of the title cyclobutanes (GC/FI ratio: Σ cyclobutanes/decane=1·096; *endo* Diels–Alder/decane=0·51), 12 mg (0·094 mmol) of DCB, 41 mg (0·277 mmol) of the trap triene (triene/decane=2·9), 15 mg (0·105 mmol) of decane and 2 ml of CH_3CN. After 6 h of photolysis, the following ratios were determined from electronic integrations of a gas chromatogram (GC/FI) of the products: Σ cyclobutanes/decane=0·515, *endo* Diels–Alder/decane=0·118 (131% increase), and triene/decane=1·153. Traces of triene dimer [M^+=296, *m/e* =148 (40%), *m/e* =92 (100%)] were observed. Cycloadduct identities were determined by GC/MS. The products were identified by GC/MS. *None* of the known triene/PVS Diels–Alder adducts nor any triene/*E,E*-2,4-hexadiene adducts were detected via GC/MS. A control reaction to demonstrate the viability of formation of the various possible cycloadducts derivable from PVS, the triene, and *E,E*-2,4-hexadiene while simultaneously present in the same reaction was then performed. To a small pyrex vial was added 74 mg (0·54 mmol) of PVS, 71 mg (0·48 mmol) of the triene, 45 mg (0·55 mmol) of *E,E*-2,4-hexadiene, 29 mg (0·23 mmol) of DCB, 66 mg (0·45 mmol) of *n*-decane (internal standard), and 2 ml of CH_3CN. All products were identified by GC/MS and quantified via GC/FI. After 7 h of photolysis, the following ratios of products were obtained: (Σ PVS/hexadiene cycloadducts)/decane=0·139, (Σ triene/hexadiene cycloadducts)/decane=0, (Σ PVS/triene cycloadducts)/decane=0·061, (Σ PVS/HD cycloadducts)/(Σ PVS/triene cycloadducts)=2·26. Small amounts

of PVS dimer were also observed. Although the triene is apparently less reactive towards PVS cation radical than *E,E*-2,4-hexadiene, its relatively high concentration during the rearrangement would more than compensate for this difference. Hence, the triene emerges an appropriate trap for this reaction.

Relative reactivities of *E*-1,3-pentadiene and *E,E*-2,4-hexadiene towards *E*-anethole cation radical

A control run to determine the relative reactivities of *E*-1,3-pentadiene and *E,E*-2,4-hexadiene towards *trans*-anethole catical was then performed. Thus 72 mg (0·45 mmol) of TA, 68 mg (1·0 mmol) of *E*-1,3-pentadiene, 84 mg (1·02 mmol) of *E,E*-2,4-hexadiene, 70 mg (0·55 mmol) of DCB, 71 mg (0·5 mmol) of *n*-decane (internal standard) and 2 ml of CH_3CN were irradiated for 6 h while in a small pyrex vial. The products were identified by GC/MS. The following ratios were determined via GC/FI analysis: (Σ 1,3-pentadiene/TA cycloadducts)/decane=0·268; (Σ 2,4-hexadiene/TA cycloadducts)/decane=0·020; (Σ 1,3-pentadiene/TA cycloadducts)/(Σ 2,4-hexadiene/TA cycloadducts)=13·4. Hence *E*-1,3-pentadiene was an appropriate trap for the study of this rearrangement.

Relative reactivities of 2,3-dimethyl-1,3-butadiene and 1,3-butadiene towards *E*-anethole cation radical

A control reaction to demonstrate the appropriateness of 2,3-dimethyl-1,3-butadiene as a trap by comparing its reactivity towards TA catical with that of 1,3-butadiene was then performed. Thus a solution of 193 mg (1·30 mmol) of TA, 421 mg (7·8 mmol) of 1,3-butadiene, 515 mg (6·3 mmol) of 2,3-dimethyl-1,3-butadiene, 185 mg (1·30 mmol) of *n*-decane (internal standard), and 5 ml DCM was cooled to −6 °C in an ice/salt bath. To the stirred solution was added 255 mg (0·31 mmol) of solid $(p\text{-BrPh})_3NSbCl_6$ as rapidly as possible. A reaction aliquot was quenched after 1 min with saturated methanolic K_2CO_3. The products were identified by GC/MS. The following ratios were determined via GC/FI analysis: (Σ 2,3-dimethyl-1,3-butadiene/TA cycloadducts)/decane=0·185, (Σ 1,3-butadiene/TA cycloadducts)/decane=0·062, (Σ 2,3-dimethyl-1,3-butadiene/TA cycloadducts)/(Σ 1,3-butadiene/TA cycloadducts)=2·98. After 10 min of reaction time, the following ratios were determined: (Σ 2,3-dimethyl-1,3-butadiene/TA cycloadducts)/decane=1·06, (Σ 1,3-butadiene/TA cycloadducts)/decane=0·280, (Σ 2,3-dimethyl-1,3-butadiene/TA cycloadducts)/(Σ 1,3-butadiene/TA cycloadducts)=3·79. Hence 2,3-dimethyl-1,3-butadiene was an appropriate trap for this rearrangement.

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