gel, it seems reasonable to postulate the hydrolysis of the phosphorus-nitrogen bond leading to *N*-hydridonitrilimine **33** and hydroxyphosphane **34**; subsequent rearrangements would give the observed products (Scheme IX).

Conclusion

Thirty years after the discovery by Huisgen of transient nitrilimines, we have shown that these 1,3 dipolar species can be isolated at room temperature. The use of bulky substituents is necessary and push-pull effects also are important. The electrophilic substitution of diazolithium salts is a new and effective synthetic method for nitrilimines. Thermal rearrangement, under mild conditions, leads to the isomeric diazo derivatives, while under irradiation nitrilimine **12** undergoes a nitrogen-nitrogen bond cleavage leading to the nitrile **19** and to the dimer of the phosphanyl nitrene **28**. This is a new route to the only known cyclodiphosphazene **20**. Regioselective [2 + 3] cycloaddition is observed with electron-poor olefins, alkynes, and with isocyanates. The absence of stereoselectivity observed with dimethyl maleate might involve a non-concerted process. The X-ray crystal study of **12** brings some evidence for the nonplanarity of nitrile imines.

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Supplementary Material Available: Tables of fractional atomic coordinates, hydrogen atomic positional and thermal parameters, and final anisotropic thermal parameters (7 pages); listings of structure factor amplitudes (26 pages). Odering information is given on any current masthead page.

Competing Hole Catalyzed Diels-Alder and Cyclobutanation/Vinylcyclobutane Rearrangement Paths. A Mechanistic Dichotomy

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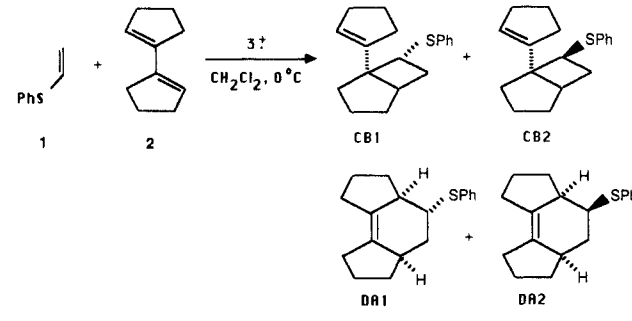
Abstract: Kinetic studies of the tris(4-bromophenyl)aminium hexachloroantimonate catalyzed cycloaddition of phenyl vinyl sulfide (**1**) and 1,1′-bicyclopentenyl (**2**) reveal three discernible stages: (1) a cycloaddition stage in which cyclobutanation predominates over Diels-Alder addition, (2) a syn/anti rearrangement stage in which the initially predominant syn cyclobutane (CB) adduct rearranges to the more stable anti isomer, and (3) a vinylcyclobutane rearrangement stage in which the anti cyclobutane isomer rearranges to the endo Diels-Alder (DA) isomer. At -30 °C, the latter rearrangement is frozen out. The variation of the initial CB/DA ratio with time, relative and absolute substrate concentrations, added triarylamine, and with electron-donating and -withdrawing substituents on the aryl ring of **1** reveals a mechanistic dichotomy in which the reaction $\mathbf{1}^{\bullet+}/\mathbf{2}$ affords primarily DA adducts and the reaction $\mathbf{2}^{\bullet+}/\mathbf{1}$ give CB adducts. Hole transfer in the ion dipole complexes $\mathbf{1}^{\bullet+}/\mathbf{2}$ and $\mathbf{2}^{\bullet+}/\mathbf{1}$ is therefore inferred to be slower than cycloaddition. Finally a competition between a hole transfer chain and a true hole catalytic reaction is inferred.

Hole-catalyzed (cation radical/neutral) cycloadditions of conjugated dienes with electron-rich dienophiles such as vinyl ethers, vinyl sulfides, and *N*-vinyl amides provide an effective strategy for cycloaddition to this normally unreactive class of dienophiles.[1-6] Although Diels-Alder (DA) periselectivity has been observed in cycloadditions of vinyl ethers and vinyl sulfides to 1,3-cyclohexadiene,[2] the addition of *N*-methyl-*N*-vinylacetamice to the latter diene is highly cyclobutane (CB) periselective,[4] and the additions of all three electron-rich dienophiles to conformationally flexible dienes yield CB adducts predominantly.[1,3] In the case of the vinyl ether and *N*-vinyl amide CB adducts, anion assisted vinylcyclobutane rearrangement strategies have been developed which provide efficient indirect synthetic routes to the corresponding Diels-Alder adducts.[3,4] In the case of the phenyl vinyl sulfide CB adducts, a hole-catalyzed vinylcyclobutane rearrangement provides similarly convenient access to net Diels-Alder addition.[5] The hole-catalyzed cycloadditions of phenyl vinyl sulfide (**1**) are especially complex because of the competition between direct and indirect Diels-Alder pathways. The present study of the hole-catalyzed cycloaddition of **1** and 1,1′-bicyclopentenyl (**2**) was undertaken to determine the relative extent of the contributions of the two discrete pathways and to establish and compare their respective stereochemical profiles. In fact the reaction system $[\mathbf{1} + \mathbf{2}]^{\bullet+}$ emerges as significantly more complex than had initially been assumed in that two distinct role-differentiated mechanisms, characterized by distinctly different CB/DA periselectivities, are observed. The results have potentially im-

Scheme I



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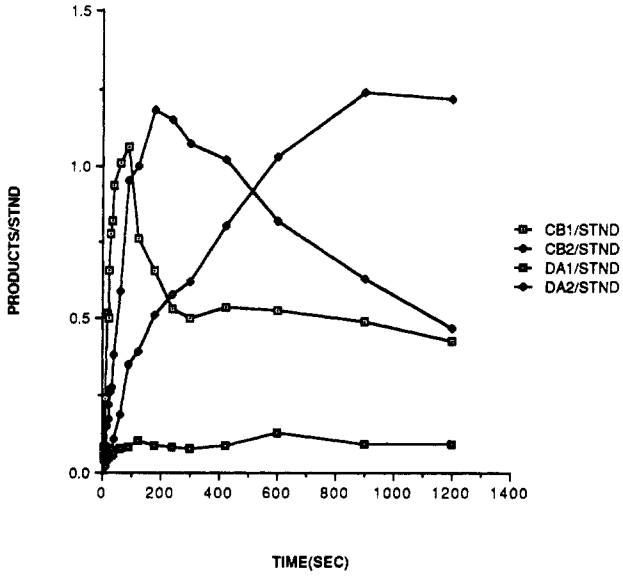

Figure 1. Rates of cycloadduct formation in the reaction of **1** and **2** (both 0.1 M) in dichloromethane at 0 °C, initiated by tris(4-bromophenyl)-aminium hexachloroantimonate ($3^{\bullet+}$; 17 mol % relative to **1** and **2**). STND = decane standard.

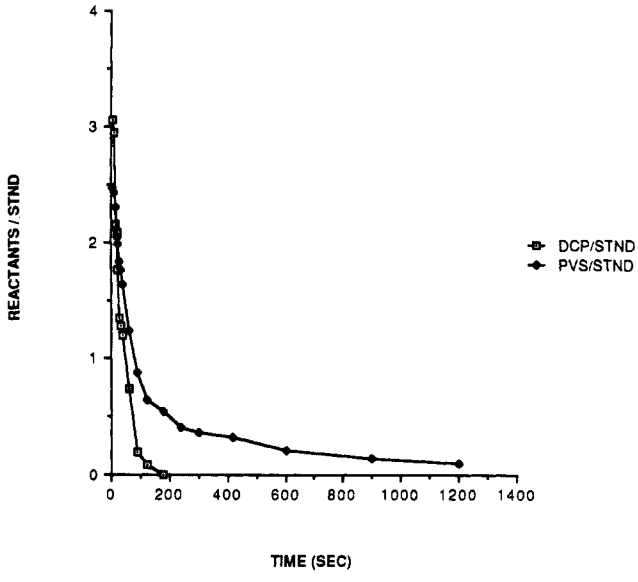

Figure 2. Rates of reactant consumption in the reaction of Figure 1.

portant implications for hole-transfer rates in cation radical/neutral pairs ("ion dipole complexes").

Results

Typical results of a kinetic study of the reaction of phenyl vinyl sulfide (**1**) and 1,1'-bicyclopentenyl (**2**) in dichloromethane (0.1 M, 1:1 molar ratio of **1**/**2**, 0 °C) catalyzed by tris(4-bromophenyl)aminium hexachloroantimonate ($3^{\bullet+}$, 17 mol %, relative to **1** and **2**) are displayed in Figure 1. This plot reveals, and studies of the decrease in reactant concentrations with time confirm (Figure 2), that the cycloaddition phase of the reaction is essentially complete within 100 s. The four observed cycloadducts, obtained in a total yield of 70%, have been identified in this work as the syn and anti cyclobutanes CB1 and CB2, respectively, and the exo and endo Diels–Alder adducts DA1 and DA2, respectively (Scheme I). In this phase of the reaction the cyclobutanes clearly predominate and the relative order of abundance at the earliest times tracked (5 s) is CB1 > CB2 > DA1 > DA2. Subsequent to this initial phase of the reaction (0–100 s), the concentration of DA1 (the exo DA adduct) remains constant, demonstrating that DA1 is not formed at all in the ensuing vinylcyclobutane rearrangement phase, but rather arises from a direct Diels–Alder addition. Evidently this latter reaction affords relatively little of

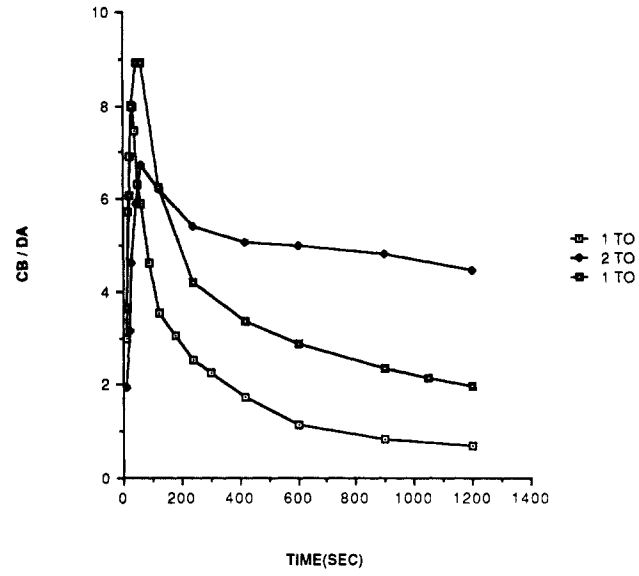

Figure 3. The CB/DA periselectivity ratio as a function of time in the reaction of Figure 1. Also, the same ratio in the analogous reactions in which the relative reactant concentrations are 2:1 and 1:2, respectively (the concentration of the minor component being held constant and equal to the common value in Figure 1). The first relative concentration given is that of **1**.

the endo Diels–Alder adduct (DA2). However this latter isomer "grows in" rapidly in the second phase and ultimately is the major product of the reaction. Evidently DA2 is the sole product of the hole-catalyzed vinyl cyclobutane rearrangement, since no DA1 is formed during this phase of the reaction. Indeed, after 200 s the only operative process is the rearrangement of CB2 to DA2. This conclusion is affirmed by a comparison of the slopes of the CB2 and DA2 plots, especially in the region of crossing (500 s). Consequently the rearrangement occurs stereoselectively via a suprafacial/retention pathway (anti CB to endo DA), in accord with observations of other hole catalyzed vinylcyclobutane rearrangements.[5] The initially preponderant syn CB (CB1) apparently does not rearrange directly to either DA adduct, but instead isomerizes to the anti CB (CB2), which subsequently rearranges to DA2. The isomerization of CB1 to CB2 may be seen to occur in the 100–200-s time frame (see crossing at 100 s).

Further mechanistic complexity is revealed by a plot of the CB/DA periselectivity ratio as a function of time (Figure 3). Though the initial CB/DA periselectivity is modest (2.99), it increases sharply until about 30 s, attaining a maximum value of 8.02 prior to decaying as a result of the CB2 to DA2 vinyl cyclobutane rearrangement. Since studies of the rate of reactant consumption revealed that **2** is consumed more rapidly than **1** (cyclodimerization of **2** is a significant competing reaction), it seemed possible that the dramatic rise in the CB/DA ratio with time in the early phase of the reaction might be correlated with a variation in the relative concentrations of **1** and **2**. Such a periselectivity dependence would be expected if dual role differentiated mechanisms having disparate CB/DA periselectivities are operative. An analogous kinetic study using an initial 2:1 ratio of **2** and **1**, respectively, does indeed reveal a substantially lower initial CB/DA ratio (1.94), which increases to a maximum value of only 6.74. Conversely, when the initial ratio of **2** to **1** is 1:2 (excess phenyl vinyl sulfide), the initial periselectivity ratio is increased to 3.63, and this rises to a maximum of 8.93. The existence of such a substantial dependence of the periselectivity ratio on the relative concentrations of **2** and **1** is important mechanistically and appears to be diagnostic of dual role differential mechanisms, as will be discussed in the following section. However, since the relative concentrations of **2** and **1** decrease in the relevant portion of the reaction (0–30 s), to no more than 1:2, the very high CB selectivities (7–10) observed during the latter stages of this reaction phase cannot be solely attributed to a relative concentration effect. Studies of the effect of the aminium salt

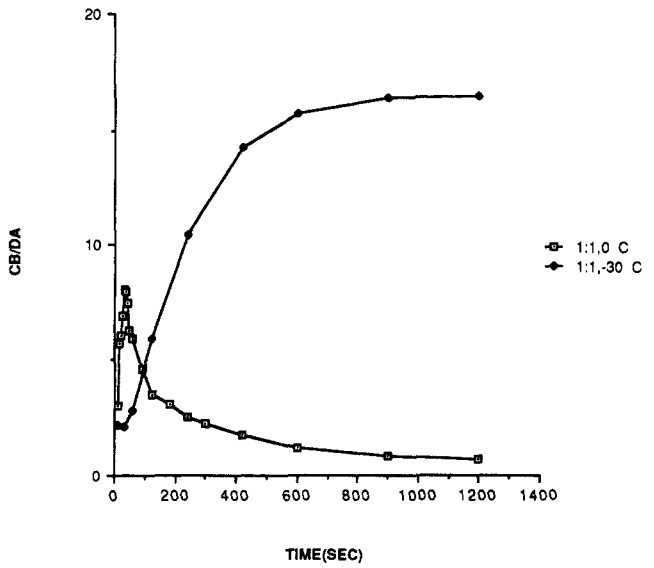

Figure 4. The CB/DA periselectivity ratio for the reaction of Figure 1, but carried out at −30 °C. Secondary rearrangements are suppressed.

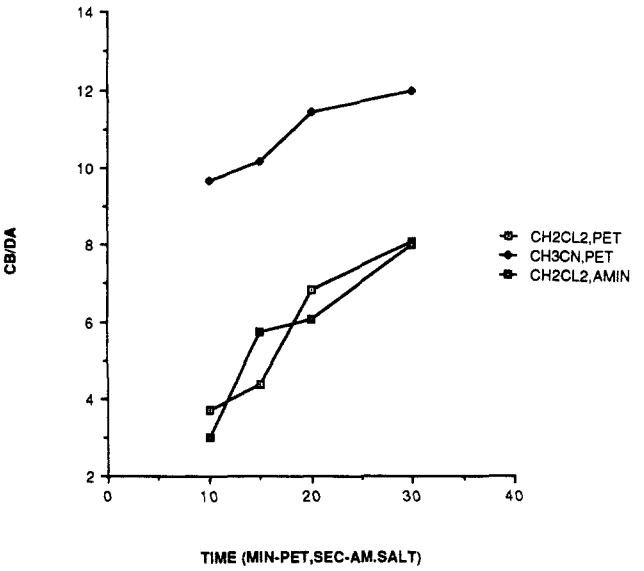

Figure 5. The CB/DA periselectivity ratio in the reaction of **1** and **2** under photosensitized electron transfer conditions (1,4-dicyanobenzene, 20 mol %; **1** and **2**, 0.3 M; acetonitrile or dichloromethane; *hν*) compared to the periselectivity ratio in the reaction of Figure 1 (AMIN = aminium salt).

($3^{\bullet+}$) concentration reveal no significant effect on the initial or maximum CB/DA ratio. However, the addition of the free triaryl amine (17 mol %) to the reaction mixture does result in further significant enhancement of the initial CB/DA ratio (to 4.63). Consequently, the gradual formation of **3**, which is expected and has been demonstrated in an earlier kinetic study,[7] must also contribute to the sharp rise in CB/DA selectivity.

The CB/DA profile is perhaps most clearly evident in a kinetic study at −30 °C, at which temperature the CB1 to CB2 and the CB2 to DA2 rearrangements are frozen out (Figure 4). Although the initial CB/DA periselectivity ratio is quite similar to that observed at 0 °C (2.19 vs 2.99), the ratio rises to a maximum of 16.5 as a result of the complete suppression of secondary rearrangements and a more CB periselective reaction. The involvement of Brønsted acid catalyzed rearrangement or decomposition at any phase of the reaction is ruled out by the stability of the cyclobutanes under these conditions, as well as by the obtention of similar results in the presence of excess 2,6-bis(*tert*-butyl)-pyridine. That the DA adduct (DA1) which is primarily formed in the early reaction phase is not the one exclusively formed by hole-catalyzed rearrangement, also negates the possibility of a hole-catalyzed rearrangement process in the early phase of the reaction, where the CB/DA ratio is low.

Under typical photosensitized electron transfer conditions (PET; 1,4-dicyanobenzene, 20 mol %, acetonitrile, pyrex, *hν*, ambient), the initial periselectivity ratio is substantially greater than in the aminium salt promoted reaction (9.68), but the periselectivity does experience the typical increase (Figure 5). However, when the PET reaction is carried out in the same solvent as the aminium salt reaction (viz. dichloromethane) the results are rather similar to those observed in the aminium salt reaction (also Figure 5).

The foregoing, and still other, kinetic studies were then used to identify conditions appropriate for the isolation and characterization of three of the four cycloadducts as the predominant cycloadduct component. The endo DA adduct (DA2), of course, is the major product after about 10 min of reaction time. When a 2:1 excess of **2** is used, the secondary rearrangements are suppressed and the major product is CB1 (the syn cyclobutane). When the aminium salt promoted reaction is carried out in the presence of the hindered base, the CB1 to CB2 rearrangement is accomplished, but the CB2 to DA2 rearrangement is suppressed (catalyst is exhausted after ca. 200 s), thus providing CB2 (the anti CB) as the major product. The exo DA adduct (DA1) was characterized by mass spectral criteria and especially by the similarity of the mass spectra of DA1 and DA2. The DA adducts exhibit much stronger parent ions than the CB adducts, in addition to peaks for $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ (the latter in the majority). Most characteristically, it has previously been shown that DA adducts of **1** have parent ions corresponding to M−PhS, in contrast to the CB adducts, which exhibit a parent ion corresponding to retrocyclobutanation (in this case $\mathbf{2}^{\bullet+}$). Cyclic adducts (both CB and DA adducts) typically have mass spectra which are relatively free of fragments in the mass region between the molecular ion and the retrocycloaddition fragments, in sharp contrast to acyclic adducts.

Table I. Half-Wave Oxidation Potentials and Initial Periselectivity Ratios in Aminium Salt Catalyzed Reactions of Substituted Aryl Vinyl Sulfides with 1,1′-Bicyclopentenyl

4-substituent	$E_{1/2}$[a]	CB/DA[b]
ethyl	1.23	0.85
hydrogen	1.33	3.02
bromo	1.38	8.74
(dicyclopentenyl)	(1.22)	

[a] Electrolyte: 0.2 M solution of n-Bu_4N ClO_4 in acetonitrile; 100 V/s; Pt/SCE. [b] After 5 s under standard conditions.

The preceding experiments appear uniquely consistent with dual role differentiated mechanisms with divergent (CB vs DA) periselectivities, but do not unambiguously elucidate which mechanism is CB and which is DA periselective. Although strong evidence on this point is available from other studies (see Discussion section), independent evidence was sought in the study of the cycloadditions of bicyclopentenyl with para-substituted aryl vinyl sulfides. The half-wave oxidation potential of *p*-ethylphenyl vinyl sulfide (**5**) was determined to be 0.10 V less than, and that of *p*-bromophenyl vinyl sulfide (**6**) 0.05 V greater than, that of phenyl vinyl sulfide (Table I). In the same electrochemical system, bicyclopentenyl was found to be somewhat more readily oxidizable than any of these (1.22 V). Kinetic studies of the cycloadditions of these aryl vinyl sulfides with bicyclopentenyl revealed reaction profiles closely analogous to those of the parent. The initial periselectivity ratios are recorded in the table and are in excellent accord with the proposition that the reaction component proceeding via aryl vinyl sulfide cation radicals is DA periselective, whereas that proceeding via bicyclopentenyl cation radicals is CB periselective.

Discussion

Kinetic studies of the aminium salt ($3^{\bullet+}$) initiated reaction of **1** and **2** distinguish three major reaction stages, viz. cycloaddition (0–100 s), syn/anti cyclobutane isomerization (100–200 s), and

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vinylcyclobutane rearrangement (>200 s). The third stage exclusively features an sr stereoselective rearrangement of the anti cyclobutane adduct (CB2) to the endo Diels–Alder adduct (DA2). Hole-catalyzed vinylcyclobutane rearrangements are now relatively well established, and the suprafacial/retention stereochemical mode appears to be the norm for these reactions.[5] As has been noted elsewhere, orbital symmetry control appears to be largely negated in hole-catalyzed reactions, thus permitting pericyclic reactions to occur via the stereochemical path which maintains the most efficient cyclic overlap. Antarafacial and invertive stereochemical elements are considered to diminish the efficiency of pericyclic overlap in small, cyclic conjugated systems such as that involved in the vinylcyclobutane rearrangement transition state.

The isomerization of an initially (kinetically) favored syn cyclobutane (CB1) to the thermodynamically more favorable anti isomer (CB2), encountered in the second stage, is also well precedented.[8] The fact that this isomerization is faster than a potentially competing vinylcyclobutane rearrangement to DA1 (or DA2) is noteworthy but also has precedent.[9] This isomerization is presumed to proceed via cleavage of the weakest cyclobutane bond of $CB1^{\bullet+}$ to give an acyclic cation radical which can undergo appropriate single bond rotation and reclosure to $CB2^{\bullet+}$. Since DA adducts are apparently not significantly produced in this reaction, it is presumed that the cleavage primarily involves the s-trans conformer of $CB1^{\bullet+}$, which cleaves to an acyclic intermediate which is geometrically unable to cyclize to a DA adduct. The opposite behavior of $CB2^{\bullet+}$, viz. rearrangement faster than isomerization, is plausible on the basis of the contrathermodynamic nature of the required isomerization, but may also involve other factors such as a larger s-cis conformational population of CB2 than CB1 and/or selective stabilization of the transition state leading to the endo product (e.g., by interaction of the phenylthio hole site with the endo double bond).

The cycloaddition stage of the reaction exhibits the preference for cyclobutanation over Diels–Alder addition expected for the reaction of a conformationally flexible diene with an electron rich dienophile.[1,3] The analogous reactions of **2** with ethyl vinyl ether and with *N*-methyl-*N*-vinylacetamide, for example, are 98 and 100% CB periselective, respectively. These latter cycloadditions almost certainly proceed in the mechanistic role sense $\mathbf{2}^{\bullet+}$/dienophile.[4] Since **2** may be assumed to exist predominantly in the s-trans conformation, *s-trans*-$\mathbf{2}^{\bullet+}$ must be primarily involved. The latter, of course, can not directly undergo Diels–Alder addition, and the high barrier to rotation around the central bond of a diene cation radical precludes isomerization to *s-cis*-$\mathbf{2}^{\bullet+}$. In the latter phases of the cycloaddition stage of the reaction of **1** and **2**, an analogously high CB periselectivity is indeed observed, especially when the secondary rearrangements are "frozen out" (−30 °C). Thus, the uniqueness of the present reaction system is the relatively low (3:1) CB/DA periselectivity which is exhibited in the early part of the reaction. This feature is reproduced under all conditions of temperature, concentrations of **1**, **2**, $\mathbf{3}^{\bullet+}$, and **3**, in the presence of a hindered base, and even qualitatively under photochemical electron transfer conditions, especially in dichloromethane solvent. Although the low CB/DA selectivity phase of the cycloaddition normally accounts for only about 10% of the total cycloaddition process, this is extended to ca. 20% in the presence of excess **2**. Finally, since the DA adduct which is almost solely responsible for the low CB/DA periselectivity in the initial phase of cycloaddition (viz. DA1) is not formed at all in the subsequent vinylcyclobutane rearrangement, its formation cannot be attributed to an indirect hole-catalyzed path.

In view of the relatively small difference in the oxidation potentials of **1** and **2** (1.33 and 1.22 V vs SCE, respectively; 0.11 V = 2.54 kcal/mol), it was considered possible that the reaction system $[\mathbf{1} + \mathbf{2}]^{\bullet+}$ might be exceptionally amenable to mechanistic role duality. Thus, the reaction mode which would be expected to predominate ($\mathbf{2}^{\bullet+}/\mathbf{1}$) might be accompanied, in this system, by its role reversed counterpart ($\mathbf{1}^{\bullet+}/\mathbf{2}$). If the latter mechanism were characterized by DA selectivity, or at least CB selectivity much more modest than the former, the present results could be comfortably accommodated. Thus, a mixture of two mechanisms having opposed, or at least sharply constrasting, periselectivities would explain the modest CB periselectivities observed initially, while the suppression of the less CB selective mechanism at later reaction times would rationalize the exclusive CB periselectivity observed in the latter part of the cycloaddition. It is therefore critical to address the question of the periselectivity of the $\mathbf{1}^{\bullet+}/\mathbf{2}$ mechanism. Recent results from a study of the hole-catalyzed cycloadditions of electron-rich dienophiles to 4-isopropenyl-1-vinylcyclohexene (**4**) are especially illuminating. In typical fashion for a conformationally flexible diene, **4** reacts with ethyl vinyl ether and with *N*-methyl-*N*-vinylacetamide with 100% CB periselectivity. The mechanisms of these reactions have been clearly diagnosed as of the $\mathbf{4}^{\bullet+}$/dienophile type.[5] In contrast, the reaction of **1** with **4** yields cycloadducts with >90% DA periselectivity. Since **1** is the only one of the series of electron rich dienophiles which is more readily ionized than **4** ($E_{1/2}$ 1.52 V), its contrasting cycloaddition periselectivity is ascribed to the operation of a unique mechanism ($\mathbf{1}^{\bullet+}/\mathbf{4}$). The greater DA selectivity of such a mechanism appears quite plausible on the basis that the conformational barrier in the neutral diene (in sharp contrast to that of the diene cation radical) is quite modest (ca. 2–5 kcal/mol) and could easily permit isomerization to the s-cis diene conformation necessary for Diels–Alder addition. Further, although orbital symmetry effects now appear to be minimal in hole-catalyzed reactions, it might be formally noted that a Diels–Alder addition of the type $\mathbf{1}^{\bullet+}/\mathbf{4}$ is of the symmetry allowed [4 + 1] type, whereas a DA addition of the type $\mathbf{4}^{\bullet+}/\mathbf{1}$ (or $\mathbf{2}^{\bullet+}/\mathbf{1}$) is of the symmetry forbidden [3 + 2] type.[1,10,11]

The unique periselectivity profile of the $[\mathbf{1} + \mathbf{2}]^{\bullet+}$ reaction is therefore plausibly rationalized in terms of mechanistic role duality. Direct experimental evidence for this interpretation is expressed in the pronounced dependence of the periselectivity ratio upon the relative concentrations of **1** and **2**. Thus excess **2** diminishes the CB periselectivity ratio, favoring the more DA selective $\mathbf{1}^{\bullet+}/\mathbf{2}$ mechanism, while excess **1** increases the CB/DA ratio, favoring the more CB selective $\mathbf{2}^{\bullet+}/\mathbf{1}$ mechanism. Intuitively, the qualitative sense of these effects may or may not appear to be correct. Indeed, a priori, either the observed sense or its opposite is possible, depending upon the relative magnitudes of four rate constants (see Appendix). The relative complexity arises as a consequence of the competing dimerizations ($\mathbf{2}^{\bullet+}/\mathbf{2}$ and $\mathbf{1}^{\bullet+}/\mathbf{1}$). The experimentally observed sense is that expected when the dimerization rate constants (for the $\mathbf{2}^{\bullet+}/\mathbf{2}$ and $\mathbf{1}^{\bullet+}/\mathbf{1}$ reactions) are greater than the cross addition rate constants ($\mathbf{1}^{\bullet+}/\mathbf{2}$ and $\mathbf{2}^{\bullet+}/\mathbf{1}$, respectively).

The sharp increase in the CB/DA periselectivity ratio during the reaction is not, however, engendered exclusively by the increase in the [1]/[2] ratio. Rather, it is also affected by the development of modest concentrations of the triarylamine. Indeed, initial periselectivity ratios CB/DA > 7 are observed when the initial ratio [1]/[2] = 2, the initial concentration of triarylamine is 0.01 M, and the initial total concentration of **1** + **2** = 0.09 M, all corresponding to values these variables attain in a typical reaction in the highly CB periselective portion of the reaction. The profile of these effects points to a clear rationale for the variable CB/DA ratios. The CB/DA periselectivity depends, among other things, on the relative rates of generation of $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ and is thus dependent on the specific hole-transfer agent which ionizes **1** and **2**. In the hole-transfer chain (HTC) mechanism, exoergic hole

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transfer from an adduct cation radical ($A^{\bullet+}$) should generate $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ relatively unselectively. However, in a true HT catalytic process, the hole-transfer agent which ionizes **1** and **2** is the aminium ion. The latter hole transfer is strongly endothermic and should be much more selective in generating $\mathbf{2}^{\bullet+}$ and thus favoring cyclobutanation. Higher concentrations of triarylamine should, of course, favor this latter process by intercepting the adduct cation radicals. Lower total concentrations of [**1**] + [**2**] should also favor this catalytic process. Consequently, the consistent and satisfying picture emerges that a hole transfer chain mechanism of low CB/DA periselectivity dominates in the early stages of the reaction where the [Ar_3N] is low and the [**1** + **2**] is high, but a true catalytic process of high CB periselectivity begins to compete and then dominate as the [Ar_3N] increases and [**1** + **2**] decreases.

The observation that *p*-ethylphenyl vinyl sulfide (**5**), a substrate more ionizable than the parent phenyl vinyl sulfide (Table I), gives increased amounts of Diels–Alder adducts (i.e., decreased CB/DA ratios) while *p*-bromophenyl vinyl sulfide (**6**), a substrate less ionizable than the parent, gives increased amounts of cyclobutane adducts (i.e., increased CB/DA ratios) provides substantial further support for the novel concept of dual role differentiated mechanisms with distinct periselectivities. Moreover, these results confirm the assignment of the mechanism leading to predominant DA adduct formation as $\mathbf{1}^{\bullet+}/\mathbf{2}$ and that leading to predominant CB formation as $\mathbf{2}^{\bullet+}/\mathbf{1}$.

The existence of competing role-differentiated hole-catalyzed mechanisms is of special interest in relation to the phenomenon of hole transfer. The existence of two such reaction paths which remain discrete all the way to products implies that cycloaddition is faster than hole transfer. Such a circumstance is unprecedented but by no means implausible, given that hole transfer requires substantial solvent and internal reorganization energy.[16] Specifically, eq 1 (with $\Delta G_0^{\ddagger} = 7$) predicts that exoergic hole transfer between $\mathbf{1}^{\bullet+}/\mathbf{2}$ has $\Delta G^{\ddagger} = 5.8$ kcal/mol. Assuming that the

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}(1 + \Delta G_0'/\Delta G_0^{\ddagger})^2 \qquad (1)$$

maximum hole transfer rate in a contact cation radical/neutral pair (ion dipole complex) is 10^{13} mol^{-1} s^{-1},[16] the rate of hole transfer in the $\mathbf{1}^{\bullet+}/\mathbf{2}$ contact pair is 2.2×10^8, which is comparable to that of typical hole-catalyzed cycloadditions in dichloromethane (e.g., the cyclohexadiene cation radical/cyclohexadiene cycloaddition rate is 3×10^8). The assignment of $\Delta G_0^{\ddagger} = 7$ does appear to be at least approximately valid and any error would appear likely to be in the sense of underestimation. Consequently, the value $\Delta G_0^{\ddagger} = 7$ kcal/mol should be a minimum value and the calculated hole transfer rate an upper limit. In addition, the value of $\Delta G_0'$ is subject to considerable uncertainty. It will be of considerable interest to test the limits of slow hole transfer as the reaction exoergicity ($\Delta G_0'$) is increased.

Conclusions

Two distinct role differentiated mechanisms potentially exist for the hole-catalyzed cycloadditions of conjugated dienes with electron-rich alkenes. Discrete role-differentiated mechanisms are demonstrated experimentally for the first time in the cycloaddition of phenyl vinyl sulfide (**1**) and 1,1′-bicyclopentenyl (**2**). The mechanisms are distinguished by their disparate periselectivities, the $\mathbf{1}^{\bullet+}/\mathbf{2}$ mechanism being DA periselective while the $\mathbf{2}^{\bullet+}/\mathbf{1}$ mechanism is highly CB periselective. These observations establish that exoergic hole transfer within a cation radical/neutral complex can be slower than cycloaddition. The existence of competing hole-transfer chain and hole-transfer catalytic cycloaddition mechanisms is also demonstrated for the first time.

Experimental Section

Analytical gas chromatographic (GC) analyses were performed on a Varian Model 3700 equipped with a flame ionization detector and a 12-m BP 1 capillary column using nitrogen as a carrier gas. GC yields were calculated with the aid of a Hewlett-Packard 3390 A reporting integrator.

Gas chromatography/mass spectra (GC/MS) were obtained on a Finnigan MAT 4023 instrument using a 20-m DB5 capillary column and helium as carrier gas.

Proton magnetic resonance spectra were determined on a General Electric QE-300 spectrometer as solutions in $CDCl_3$. Chemical shifts are reported in parts per million downfield from the internal reference tetramethylsilane.

Methylene chloride and HPLC grade acetonitrile were distilled from phosphorus pentoxide prior to use. Acetonitrile was stored over molecular sieves prior to use, and only freshly distilled methylene chloride was used. Tris(4-bromophenyl)aminium hexachloroantimonate (Aldrich) was washed with anhydrous ether and dried in vacuo prior to use.

General Triarylaminium Salt Procedure. A solution of 1,1′-bicyclopentenyl, phenyl vinyl sulfide, and decane (standard) in anhydrous methylene chloride was cooled to 0 or −30 °C under a nitrogen atmosphere. Tris(4-bromophenyl)aminium hexachloroantimonate was added and the solution stirred. The reaction was quenched by placing 0.5 mL of a standard solution of sodium methoxide in methanol in a 3-mL syringe. This syringe was then used to withdraw a 0.25-mL aliquot from the reaction mixture. At later reaction times the reaction mixture was pipeted into the quenching solution. Aliquots were taken at approximately 10-s intervals for the first minute of reaction, 15-s intervals for the second minute, and 30–120-s intervals thereafter. The reactions were examined for a total of 15 to 20 min. The crude reacton mixtures were then analyzed by GC.

Product Analysis. Analyses of the product mixtures were carried out by GC/MS. The distinction between the DA and CB adducts has been described elsewhere, but essentially the DA adducts give strong molecular ions and a major M − PhS fragmentation.[18,19] The CB adducts give very weak molecular ions, minor amounts of M − PhS fragmentation and major retrocyclobutanation fragmentation ($\mathbf{1}^{+}$, $\mathbf{2}^{+}$). In the case of the reactions of **1** and **2**, these assignments were confirmed by isolation. The assignment of syn and anti structures to the CB adducts has also been described and is based upon a very reliable NMR chemical shift criterion (the hydrogen α to the phenylthio substituent is more upfield in the anti isomer).[18] The assignment of exo and endo structures to the Diels–Alder adducts is based upon the NMR coupling pattern of the α proton.[18]

Cycloaddition Reaction of 1,1′-Bicyclopentenyl (2) and Phenyl Vinyl Sulfide (1). A solution of 1,1′-bicyclopentenyl (**2**, 0.101 g, 0.75 mmol) and phenyl vinyl sulfide (**1**, 0.112 g, 0.82 mmol) in anhydrous dichloromethane (5.7 mL) was cooled to 0 °C in an ice bath. Tris(4-bromophenyl)aminium hexachloroantimonate ($\mathbf{3}^{\bullet+}$, 0.104 g, 0.13 mmol, 17 mol % of **2**) was added with stirring. Quenching was done as described previously. Analysis of the crude mixtures indicated the product and reactant composition as shown in Figures 1 and 2.

Cycloaddition Reaction of Excess 1,1′-Bicyclopentenyl (2) and Phenyl Vinyl Sulfide (1). A solution of 1,1′-bicyclopentenyl (**2**, 0.218 g, 1.6 mmol) and phenyl vinyl sulfide (**1**, 0.107 g, 0.79 mmol) in anhydrous dichloromethane (5.7 mL) was cooled to 0 °C in an ice bath. Tris(4-bromophenyl)aminium hexachloroantimonate ($\mathbf{3}^{\bullet+}$, 0.113 g, 0.14 mmol, 17 mol % of **1**) was added with stirring. Quenching was done as described previously. Analysis of the crude mixtures indicated the product composition as shown in Figure 3.

Cycloaddition Reaction of 1,1′-Bicyclopentenyl (2) with Excess Phenyl Vinyl Sulfide (1). A solution of 1,1′-bicyclopentenyl (**2**, 0.104 g, 0.77 mmol) and phenyl vinyl sulfide (**1**, 0.2203 g, 1.5 mmol) in anhydrous dichloromethane (5.7 mL) was cooled to 0 °C in an ice bath. Tris(4-bromophenyl)aminium hexachloroantimonate ($\mathbf{3}^{\bullet+}$, 0.104 g, 0.13 mmol, 17 mol % of **2**) was added with stirring. Quenching was done as described previously. Analysis of the crude mixtures indicated the product composition as shown in Figure 3.

Cycloaddition Reaction of 1,1′-Bicyclopentenyl (2) and Phenyl Vinyl Sulfide (1) at −30 °C. A solution of 1,1′-bicyclopentenyl (**2**, 0.105 g, 0.78 mmol) and phenyl vinyl sulfide (**1**, 0.107 g, 0.79 mmol) in anhydrous dichloromethane (5.7 mL) was cooled to −30 °C in calcium chloride solution/dry ice bath. Tris(4-bromophenyl)aminium hexachloroantimonate ($\mathbf{3}^{\bullet+}$, 0.106 g, 0.13 mmol, 17 mol % of **2**) was added with stirring. Quenching was done as described previously. Analysis of the crude mixtures indicated the product composition as shown in Figure 4.

Cycloaddition of 1,1′-Bicyclopentenyl (2) and Phenyl Vinyl Sulfide (1) via Photoinduced Electron Transfer Reaction (PET) in Acetonitrile. A solution of 1,1′-bicyclopentenyl (**2**, 0.322 g, 2.4 mmol), phenyl vinyl sulfide (**1**, 0.301 g, 2.21 mmol), and 1,4-dicyanobenzene (0.050 g, 0.39

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mmol) in dried acetonitrile (8.0 mL) was placed in a 50-mL Pyrex test tube. The tube was sealed with a rubber septum, degassed with dry nitrogen, and placed in a cooled water bath against the outside of the cooling jacket of a medium-pressure mercury vapor lamp and irradiated. Analysis of the crude reaction mixtures indicated the product composition as shown in Figure 5.

Cycloaddition of 1,1'-Bicyclopentenyl (2) and Phenyl Vinyl Sulfide (1) via Photoinduced Electron Transfer Reaction (PET) in Dichloromethane. A solution of 1,1'-bicyclopentenyl (**2**, 0.157 g, 1.17 mmol), phenyl vinyl sulfide (**1**, 0.150 g, 1.10 mmol), and 1,4-dicyanobenzene (0.025 g, 0.20 mmol) in anhydrous dichloromethane (3.6 mL) was placed in a 50-mL Pyrex test tube. The tube was sealed with a rubber septum, degassed with dry nitrogen, and placed in a cool water bath against the outside of the cooling jacket of a medium-pressure mercury vapor lamp and irradiated. Analysis of the crude reaction mixtures indicated the product composition as shown in Figure 5.

Synthesis of *endo*-2,3-*cis*-Cyclopentano-4-(phenylthio)bicyclo-[4.3.0]-1-nonene (DA2). A solution of 1,1'-bicyclopentenyl (**2**, 0.043 g, 0.32 mmol) and phenyl vinyl sulfide (**1**, 0.042 g, 0.31 mmol) in anhydrous dichloromethane (2.0 mL) was cooled to 0 °C in an ice bath. Tris(4-bromophenyl)aminium hexachloroantimonate ($3^{\bullet+}$, 0.049 g, 0.06 mmol, 19 mol % of **2**) was added with stirring. After 10 min an additional 0.017 g (6.5 mol %) of $3^{\bullet+}$ was added. The reaction was quenched after 15 min by addition of 3 mL of saturated NaOMe/MeOH solution. Analysis of the crude reaction mixture by GC indicates the presence of four different cross addition products in the ratio of 74:12:11:3 (endo/syn/exo/anti), along with some DCP dimer. The crude reaction mixture was concentrated in vacuo, and the insoluble materials were precipitated by the addition of pentane. Evaporation of the solvent followed by chromatography over silica gel (hexane) afforded 10 mg of cycloadducts (24%). The major product was shown by ^{1}H NMR and GCMS to be the endo Diels–Alder isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44–7 (m, 5 H), 3.59 (ddd, J = 11, 5, 4 Hz, 1 H), 2.60–0.82 (m, 16 H); mass spectrum, m/e 270 (M^+), 161 (P), 160, 134, 91, 67, 41; HRMS calcd for DA2, $C_{18}H_{22}S$, 270.144223, found 270.145482.

Synthesis of *syn*-1-(1-Cyclopentenyl)-7-(phenylthio)bicyclo[3.2.0]heptane (CB1). A solution of 1,1'-bicyclopentenyl (**2**, 0.133 g, 0.996 mmol) and phenyl vinyl sulfide (**1**, 0.070 g, 0.52 mmol) in anhydrous dichloromethane (3.7 mL) was cooled to 0 °C in an ice bath. Tris(4-bromophenyl)aminium hexachloroantimonate ($3^{\bullet+}$, 0.074 g, 0.09 mmol, 17 mol % of **1**) was added with stirring. The reaction was quenched after 6.5 min by addition of 4 mL of saturated NaOMe/MeOH solution. Analysis of the crude reaction mixture by GC indicates the presence of four different cross addition products in the ratio of 60:19:12:9 (syn/anti/exo/endo), along with some DCP dimer. The crude reaction mixture was concentrated in vacuo, and the insoluble materials were precipitated by the addition of pentane. Evaporation of the solvent followed by chromatography over silica gel (hexane) afforded 20 mg of cycloadducts (23%). The major product was shown by ^{1}H NMR and GCMS to be the syn cyclobutane isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55–7.11 (m, 5 H), 5.35 (m, 1 H), 3.96 (t, J = 9.0 Hz, 1 H), 2.85–0.82 (M, 15 H); mass spectrum, m/e 270 (M^+), 161, 160, 134 (P), 91, 67, 41; HRMS calcd for CB1, $C_{18}H_{22}S$, 270.144223, found 270.143709.

Synthesis of *anti*-1-(1-Cyclopentenyl)-7-(phenylthio)bicyclo[3.2.0]-heptane (CB2). A solution of 1,1'-bicyclopentenyl (**2**, 0.060 g, 0.45 mmol), phenyl vinyl sulfide (**1**, 0.059 g, 0.43 mmol), and 2,6-di-*tert*-butylpyridine (0.050 g, 0.26 mmol, 58 mol % of **2**) in anhydrous dichloromethane (2.8 mL) was cooled to 0 °C in an ice bath. Tris(4-bromophenyl)aminium hexachloroantimonate ($3^{\bullet+}$, 0.179 g, 0.22 mmol, 49 mol % of **2**) was added with stirring. The reaction was quenched after 7 min by addition of 4 mL of saturated NaOMe/MeOH solution. Analysis of the crude reaction mixture by GC indicates the presence of three different cross addition products in the ratio of 57:26:16 (anti/endo/syn), along with a trace amount of the exo adduct and some DCP dimer. The crude reaction mixture was concentrated in vacuo, and the insoluble materials were precipitated by the addition of pentane. Evaporation of the solvent followed by chromatography over silica gel (hexane) afforded 14 mg of cycloadducts (12%). The major product was shown by ^{1}H NMR and GCMS to be the anti cyclobutane isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55–7.11 (m, 5 H), 5.35 (m, 1 H), 2.98 (t, J = 7.0 Hz, 1 H), 2.85–0.82 (m, 15 H); mass spectrum, m/e 270 (M^+), 161, 160, 134 (P), 91, 67, 41; HRMS calcd for CB2, $C_{18}H_{22}S$, 270.144223, found 270.144435.

Characterization of *exo*-2,3-*cis*-Cyclopentano-4-(phenylthio)bicyclo-[4.3.0]-1-nonene (DA1). Although not isolated in pure form because at reaction times corresponding to reasonable conversion it is a minor product, DA1 is well enough characterized by its mass spectrum (essentially identical with DA2 and quite distinct from CB1 and CB2) and by its HRMS: calcd for $C_{18}H_{22}S$ 270.144223, found 270.142542.

***p*-Ethylphenyl Vinyl Sulfide (5).** A solution of (*p*-ethylphenyl)magnesium bromide from *p*-bromoethylbenzene (8.51 g, 0.046 mol) and magnesium turnings (1.92 g, 0.08 mol) in tetrahydrofuran (60 mL) was added over a 10-min period to a vigorously stirred solution of 2-chloroethyl thiocyanate (4.84 g, 0.04 mol) obtained from 1-bromo-2-chloroethane and potassium thiocyanate.[19] The reaction temperature was kept below 40 °C by occasional cooling. Stirring was continued for 15 min after the completion of the original addition, whereupon potassium *tert*-butoxide (9.0 g, 0.08 mol) in tetrahydrofuran (15 mL) was added, keeping the reaction temperature below 55 °C by occasional cooling. After a further 20 min of reaction time, the mixture was worked up by careful addition of saturated ammonium chloride solution (40 mL). The upper layer was separated and combined with the ethereal extracts of the aqueous phase. After drying over magnesium sulfate, the solvents were removed under reduced pressure. Vacuum distillation of the residue gives the product as a colorless liquid (4.1 g, 62.5 % yield): bp 96–98 °C (7 Torr); ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.22–1.27 (t, 3 H), 2.55–2.63 (q, 2 H), 5.15–5.25 (m, 2 H), 6.40–6.50 (dd, 1 H), 7.08–7.13 (d, 2 H), 7.23–7.28 (d, 2 H); ^{13}C NMR (360 MHz, $CDCl_3$) δ 15.4, 28.5, 114.2, 128.7, 130.6, 131.3, 132.7, 143.7; HRMS calcd $C_{10}H_{12}S$ 164.065972, found 164.065392.

***p*-Bromophenyl Vinyl Sulfide.** This substrate was prepared exactly as in the case of the *p*-ethyl derivative, by using 1,4-dibromobenzene (18.86 g, 0.08 mol) and magnesium (2.1 g, 0.088 mol) in tetrahydrofuran (80 mL). Correspondingly, 6.08 g (0.05 mol) of 1-bromo-2-chloroethane was used to form the isocyanate, and 8.0 g (0.07 mol) of potassium *tert*-butoxide in 15 mL of tetrahydrofuran was used for the in situ elimination. The product (3.0 g) was obtained in 28% yield: bp 98–98.5 °C (1.2 Torr); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.33–5.40 (M, 2 H), 6.42–6.51 (dd, 1 H), 7.19–7.22 (d, 2 H), 7.40–7.43 (d, 2 H); ^{13}C NMR δ 116.5, 121.0, 130.9, 131.6, 132.1, 133.5; HRMS calcd for C_8H_7BrS 213.945183, found 213.946181.

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Appendix

The rate of the $2^{\bullet+}/1$ reaction (R_{21}; rate constant k_{21}) in competition with the dimerization reaction $2^{\bullet+}/2$ (rate constant k_{22}), assuming formation of $2^{\bullet+}$ from the reaction $3^{\bullet+} + 2$ (rate constant k_{i2}) is given by eq 1, where F_2, the fraction of $2^{\bullet+}$ which reacts with **1**, is given by eq 2:

$$R_{21} = k_{i2}[3^{\bullet+}][2]F_2 \quad (1)$$

$$F_2 = k_{21}[1]/(k_{21}[1] + k_{22}[2]) \quad (2)$$

Analogously, the rate of the $1^{\bullet+}/2$ reaction (R_{12}; rate constant k_{12}) in competition with the dimerization $1^{\bullet+}/1$ (k_{11}) is given by eqs 3 and 4:

$$R_{12} = k_{i1}[3^{\bullet+}][1]F_1 \quad (3)$$

$$F_1 = k_{12}[2]/(k_{12}[2] + k_{11}[1] \quad (4)$$

The ratio of the two rates is then given by eqs 5 and 6:

$$R_{21}/R_{12} = (k_{i2}/k_{i1})(k_{21}/k_{12})(F_2'/F_1') \quad (5)$$

$$F_2'/F_1' = (k_{12}[2] + k_{11}[1])/(k_{21}[1] + k_{22}[2]) \quad (6)$$