Cation Radical Pericyclic Reactions

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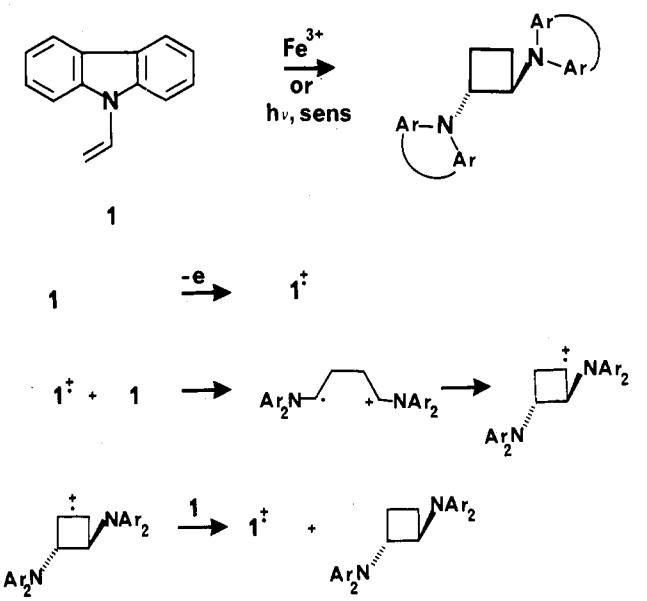
Cation Radical Pericyclic Reaction Precedents. The Cation Radical Chain Mechanism. In 1969, the cycloaddition (in 70% yield) of *N*-vinylcarbazole (**1**) catalyzed by ferric, ceric, or cupric salts in methanol was observed, and the cation radical chain mechanism depicted in Scheme I was postulated.[1] Later, a photosensitized electron transfer (PET) initiated version of the reaction was developed by the same group.[2] The prototypical exemplification of the cation radical chain Diels–Alder reaction (of 1,3-cyclohexadiene, **2**) was reported in the same year (Scheme II).[3,4] Apparently, these observations of cation radical pericyclic reactions were not broadly interpreted in terms of a potential generic reaction type of cation radicals or of possible synthetic utility.

The Aminium Salt Initiated Cation Radical Diels–Alder Reaction. In 1981, this laboratory reported observations which focused attention of the generic character of cation radical cycloadditions and of the cation radical Diels–Alder reaction in particular.[5-8] This research also provided an experimental procedure suitable for synthetic applications.

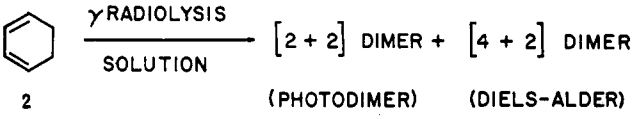
Cyclodimerization of Conjugated Dienes. The Diels–Alder cyclodimerization of 1,3-cyclohexadiene (the purely thermal version of which requires 20 h at 200 °C to achieve an optimum 30% yield) was effected in 70% yield in 5 min at 0 °C using 5 mol % (relative to **2**) of tris(4-bromophenyl)aminium hexachloroantimonate ($3^{\bullet+}$) as initiator (Scheme III).[5] That cyclodimerization is not limited to s-cis constrained dienes is evident from the cyclodimerization of 1,1′-dicyclopentenyl (**4**; 50% yield, Scheme IV).[5] The efficient cyclodimerization of 1-methyl-1,3-cyclohexadiene (**5**; 75% yield; Scheme IV) illustrates the complete regiospecificity which is consistently observed and, as well, exclusive chemoselection for the less substituted dienophilic double bond.[6]

Cross-Additions. The utility of the cation radical Diels–Alder is further enhanced by extension to cross-additions. The addition of 2,5-dimethyl-2,4-hexadiene (**6**), a sterically hindered diene which had not previously been induced to participate in a Diels–Alder addition as either the dienic or dienophilic component, with **2** (40%; Scheme V) illustrates the exceptional kinetic impetus of the cation radical Diels–Alder.[5] The analogous cycloaddition to **7** proceeds even more efficiently (90%), but with only 85% chemoselection for the less sterically hindered double bond, pointing up that even the cation radical Diels–Alder reaction is somewhat sensitive to steric effects. Addition to a methylenecyclohexene derivative (**8**) is both efficient (80%) and exclusively chemoselective for the less sterically hindered site.[6]

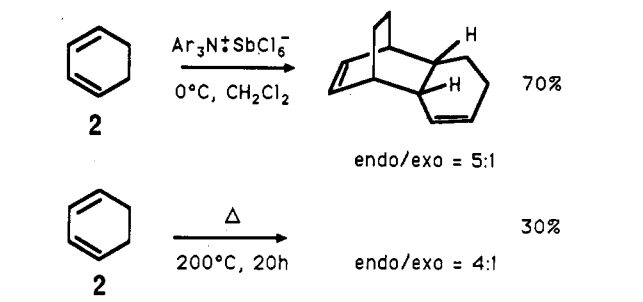
Scheme I



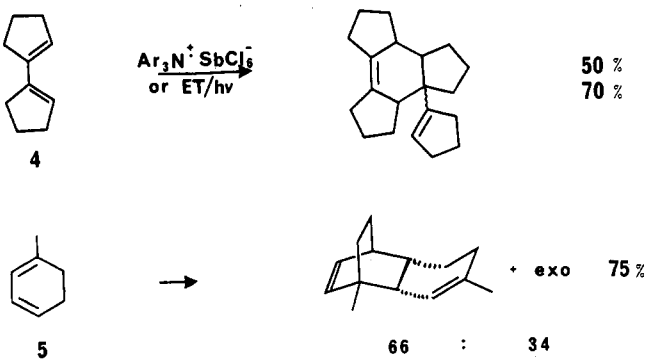
Scheme II



Scheme III



Scheme IV



The authors are all present or former members of the research group of Professor Bauld at The University of Texas at Austin. Nate Bauld is a graduate of West Virginia University (B.S., 1956) and the University of Illinois (Ph. D., 1959, E. J. Corey) and was an NSF postdoctoral research associate of Professor Paul D. Bartlett (Harvard, 1959–1960).

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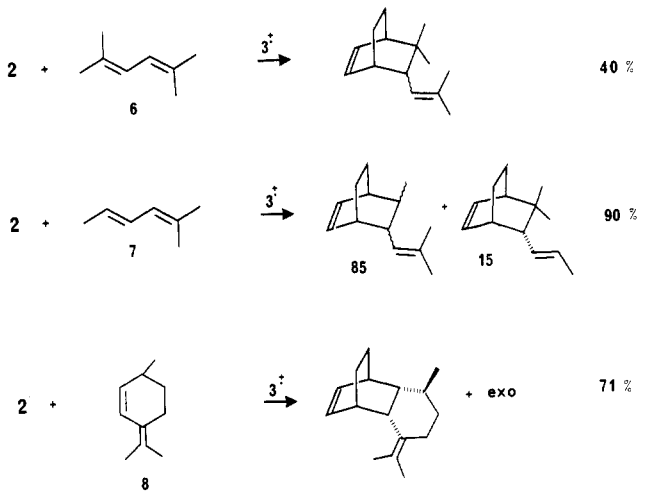
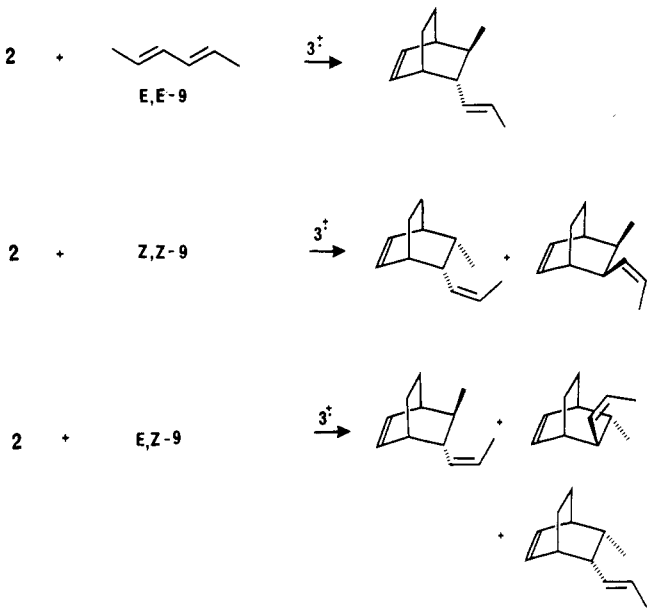
Scheme V



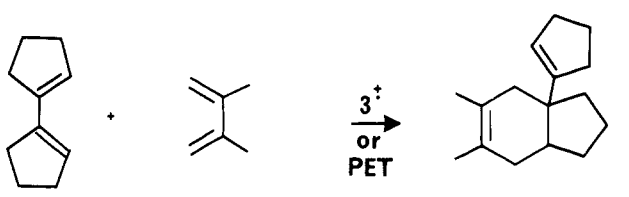
Scheme VI



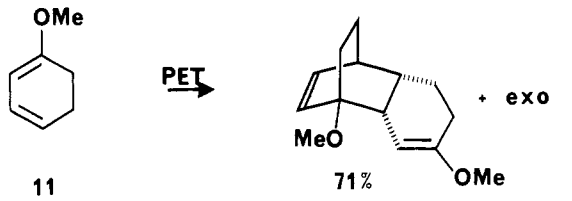
Stereospecificity and Endo Selectivity. The cross-additions of (*E*,*E*)-, (*E*,*Z*)-, and (*Z*,*Z*)-2,4-hexadiene (**9**) to **2** reveal that, like its neutral counterpart, the cation radical Diels–Alder is capable of high stereospecificity (Scheme VI).[5] The reaction with (*E*,*E*)-**9** also illustrates the impressively high (>98%) endo stereoselectivity consistently attainable when the pendant dienophilic double bond lacks a Z substituent.[5,9]

Acyclic Diene Components. Dienic components which are not cis constrained may also be amenable to the cation radical Diels–Alder, providing that they have at least modest s-cis conformational populations. Thus,

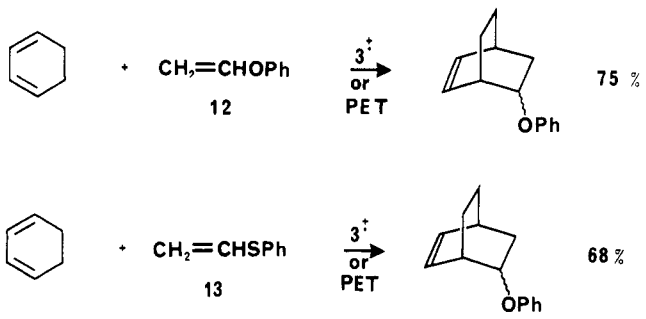
Scheme VII



Scheme VIII



Scheme IX



cycloadditions to 2,3-dimethyl-1,3-butadiene (**10**; Scheme VII) and 1,1′-dicyclopentenyl (Scheme IV) occur efficiently, but Diels–Alder additions to predominantly s-trans dienes such as 2,4-hexadiene are not as commonly encountered.

Photosensitized Electron-Transfer Initiation of the Cation Radical Diels–Alder. The PET initiation procedure, originally developed by Ledwith for cyclobutanation and refined by Farid and others,[10] was then extended to the cation radical Diels–Alder. Jones and co-workers reported the PET-initiated cyclodimerization of **2**,[11] and in the same year, the University of Texas group reported observations of a variety of cation radical Diels–Alder reactions under PET conditions and stressed the procedure as a synthetically attractive one.[8] In one example, the cyclodimerization of 1-methoxy-1,3-cyclohexadiene (**11**) was carried out on a 7.7-g scale in 50% yield (71.9%; GC) after 32 h (Scheme VIII). The cyclodimerization of **4** also occurs in significantly improved yield (71% vs 50%) under PET conditions.

The mildness of the PET procedure is also useful in extending the cation radical Diels–Alder from the diene/diene format to the diene/electron-rich alkene format (Scheme IX).[8] The reactions of phenyl vinyl ether (**12**) and phenyl vinyl sulfide (**13**) with **2** can also be accomplished under aminium salt conditions, but that between ethyl vinyl ether (**14**) and **2** cannot, again because of product instability. On the other hand, a number of cross-cycloadditions which succeed in the aminium salt protocol fail completely under PET con-

(1) (a) Bell, F. A.; Crellin, R. A.; Fugii, N.; Ledwith, A. *J. Chem. Soc., Chem. Commun.* **1969**, 251. (b) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133.
(2) Carruthers, R. A.; Crellin, R. A.; Ledwith, A. *J. Chem. Soc., Chem. Commun.* **1969**, 252.
(3) Schutte, R.; Freeman, G. R. *J. Am. Chem. Soc.* **1969**, *91*, 3715.
(4) Penner, T. L.; Whitten, D. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1979**, *101*, 2861.
(5) Bellville, D. J.; Wirth, D. D.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, *103*, 718.
(6) Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1982**, *104*, 2665.
(7) Bauld, N. L.; Pabon, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 633.
(8) Pabon, R. A.; Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1983**, *105*, 5158.
(9) Bellville, D. J.; Bauld, N. L.; Pabon, R. A.; Gardner, S. A. *J. Am. Chem. Soc.* **1983**, *105*, 3584.
(10) For a review, see: Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80.
(11) Jones, C. R.; Allman, B. J.; Mooring, A.; Spahic, B. *J. Am. Chem. Soc.* **1983**, *105*, 652.

Table I.
Half-Wave Oxidation Potentials (Ag/Ag$^+$ vs SCE, CH_3CN, Irreversible)

compound	potential
(*E*)-anethole (17)	1.11
1,1′-dicyclopentenyl	1.36
4-methyl-1,3-pentadiene	1.42
phenyl vinyl sulfide (13)	1.42
4-isopropenyl-1-vinylcyclohexene	1.52
1,3-cyclohexadiene (2)	1.53
N-methyl-*N*-vinylacetamide (15)	1.55
(*E,E*)-2,4-hexadiene (9)	1.59
ethyl vinyl ether (14)	1.60
phenyl vinyl ether (12)	1.62
(*E*)-2-methyl-1,3-pentadiene	1.70
α-methylstyrene	1.72
(*E*)-1,3-pentadiene	1.73
2,3-dimethyl-1,3-butadiene (10)	1.95
2-methyl-1,3-butadiene	1.98

ditions.[12] These cases include the cross-additions of **6** and **8** to **2**. Especially in the former case, steric effects undoubtedly retard cycloaddition and place it at a competitive disadvantage with respect to back electron transfer.[11-13]

Terminology. Discussion of the conventional Diels–Alder reaction is, of course, greatly facilitated by terminology (diene/dienophile) which distinguishes the two distinct roles involved in these reactions. Cation radical cycloadditions, in general, benefit from linguistic distinction between the cation radical and neutral roles. Since the reaction, in an overall sense, involves two neutral reactant molecules, it is also important to distinguish the role of the neutral species which generates the cation radical. In our experience, the development of such terminology is blocked by the already somewhat unwieldy nature of the term "cation radical". The terminology used in this Account represents an attempt to provide terminology which is viewed as increasingly critical to the analysis of cation radical cycloaddition mechanisms:

catical = cation radical

caticophile = neutral component which is the reaction partner of the catical

caticogen = neutral component which generates the catical

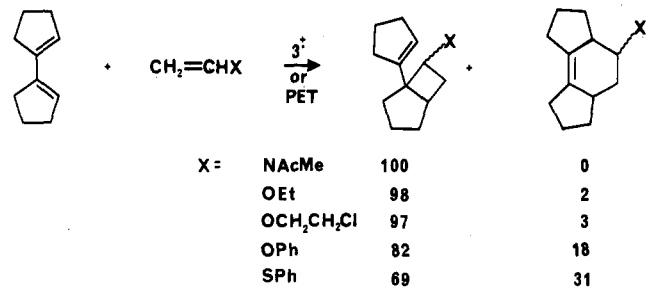
Caticogenicity (the ability to generate a catical) is assumed, roughly, to parallel the half-wave oxidation potential of the caticogen (Table I). Caticophilicity scales will tentatively and roughly be assumed to parallel π basicity or nucleophilicity.

Synthetic Strategy. The ideal circumstances for efficient catical Diels–Alder cross-cycloadditions are attained when the caticogenic and caticophilic roles are dichotomous (i.e., one neutral component is decisively more caticogenic than the second, and the latter is decisively more caticophilic than the former). However, even when the condition is not fulfilled, efficient reactions can often be achieved by the use of a 3–10-fold excess of the relatively unreactive component to suppress the offending cyclodimerization.

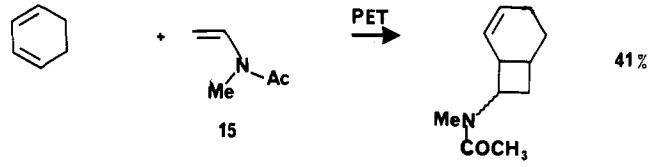
Role Selectivity. In the specific case of the catical Diels–Alder, two role-differentiated versions of the reaction have been recognized.[5,14] In one case, the catical

(12) Pabon, Jr., Raul A., unpublished research.
(13) Calhoun, G. C.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 6870.

Scheme X



Scheme XI



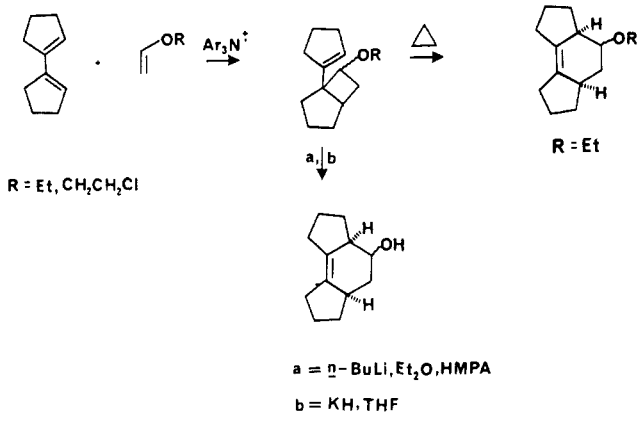
assumes the dienophilic role ([4 + 1] cycloaddition); in the other, the catical assumes the dienic role a [3 + 2] cycloaddition). The former mode is formally orbital symmetry allowed, and the latter mode is formally forbidden. Nevertheless, since the catical cyclobutanation reaction (a [2 + 1] cycloaddition) is both formally forbidden and incredibly facile, it is by no means certain that such distinctions are of overwhelming or even marginal significance. In a purely pragmatic sense, virtually all efficient catical Diels–Alder reactions observed in this laboratory appear to be of the role-normal, allowed type. This is easily verified by inspecting the reactions of Schemes VI–X (for example) and referring to the relative caticogenicities in Table I. Of course, such observations may well be fortuitous. At this juncture, the experimental evidence for role selectivity based upon inherent "allowedness" vs "forbiddenness" or relative pericyclic transition state effects is admittedly quite tenuous, but it would be unwise, from a synthetic context, to overlook the consistency of the effect, irrespective of whether it is regarded as coincidental.

Cyclobutane Periselectivity in Diene/Electron-Rich Alkene Catical Cycloadditions. In contrast to their cycloadditions to **2**, which afford predominantly Diels–Alder (DA) adducts, the catical cycloadditions of electron-rich alkenes **12–14** to acyclic dienes yield primarily cyclobutane (CB) adducts (Scheme X).[15] The product compositions are essentially independent of the initiation procedure (PET or $Ar_3N^{\bullet+}$). Reference to Table I suggests that the Diels–Alder portion of these reactions is almost certainly role-reversed. However, complete CB selectivity is also observed for simple acyclic dienes like 2,4-hexadiene, where role reversal is not strongly indicated for **12** and **14** and is counterindicated for **13**.

Enamides as Caticophiles. Most decisively, *N*-methyl-*N*-vinylacetamide (**15**), the most reactive electron-rich alkene included in the study, adds with complete CB periselectivity not only to the acyclic dienes but also to **2** (Scheme XI).[16] This result is again con-

(14) Bauld, N. L.; Bellville, D. J.; Pabon, R. A.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378.
(15) Pabon, R. A.; Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1984**, *106*, 2730.
(16) Bauld, N. L.; Harirchian, B.; Reynolds, D. W., submitted for publication in *J. Am. Chem. Soc.*

Scheme XII



firmed with both the aminium salt and PET initiator systems. The conclusion seems clear that such electron-rich alkenes (in rather sharp contrast to conjugated dienes) generally have a CB periselectivity preference which is unrelated to role effects and which is most highly developed in the enamides.

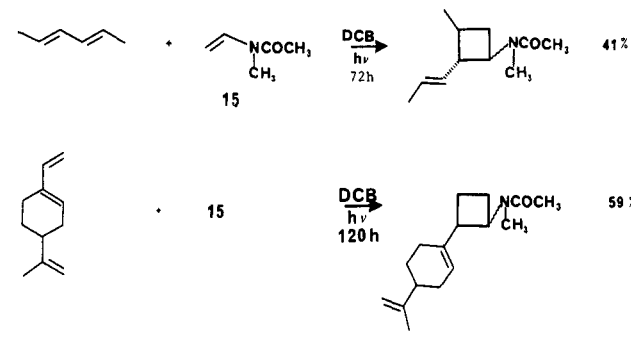
Mechanism of Cyclobutanation. These results are mechanistically quite fascinating in that they appear to preclude the possibility of an open (i.e., singly linked) catical intermediate (**16**, Scheme XXIV) in the cyclobutanation of **2** + **15**, since the latter intermediate should be able to cyclize to both DA and CB cycloadducts. These results and considerations tend strongly to support a concerted addition mechanism, possibly one involving a long-bond catical intermediate (**17**) as was earlier proposed on the basis of extended basis set ab initio SCF MO reaction path calculations for the prototype [2 + 1] cycloaddition.[17]

Cyclobutane vs Diels–Alder Periselectivity. Competitive rate studies suggest a strong correlation between experimental caticophilicity of **12–15** (toward $4^{\cdot+}$) and their CB periselectivity (Scheme X). Both of these phenomena intuitively appear to correlate roughly with substituent stabilization of a carbocation site. The proposal is, then, that the transition state leading to the long-bond intermediate (**17**) has highly developed carbocation character at the carbon atom bearing the donor substituent, as would be expected for a long-bond intermediate where catical character is concentrated in the long bond. Moreover, the carbocation character in this transition state must be greater than in the transition state leading to the Diels–Alder adduct (a circumstance certainly expected if the latter has a more synchronous nature). In further support of these proposals is the finding that α-methylstyrene adds with 100% DA periselectivity to **4**. Here, it is considered that the alkyl and phenyl substituents are, even acting together, inferior carbocation-stabilizing groups in comparison to electron pair donors such as alkoxy, phenoxy, phenylthio, and amido.

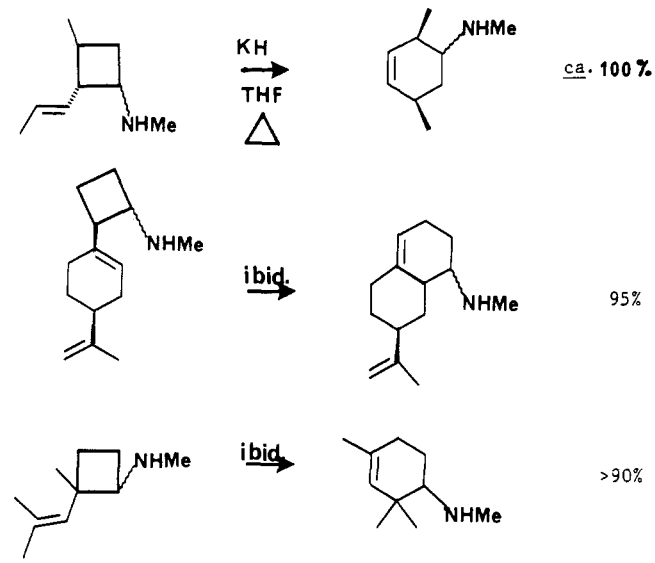
Diels–Alder Selection in Diene/Diene Format. These considerations suggest a partial rationale for the DA selectivity associated with many diene/diene catical cycloadditions, viz., the lesser carbocation-stabilizing ability of (simple) vinyl groups than heteroatom donor groups leads to a preference for the more concerted (DA) mode of addition. In addition, such diene/diene cycloadditions (unlike diene/electron-rich alkene additions)[1] virtually always have an accessible role-normal (as opposed to role-reversed) mode of cycloaddition.

(17) Pabon, R. A.; Bauld, N. L. *J. Am. Chem. Soc.* **1984**, *106*, 1145.

Scheme XIII



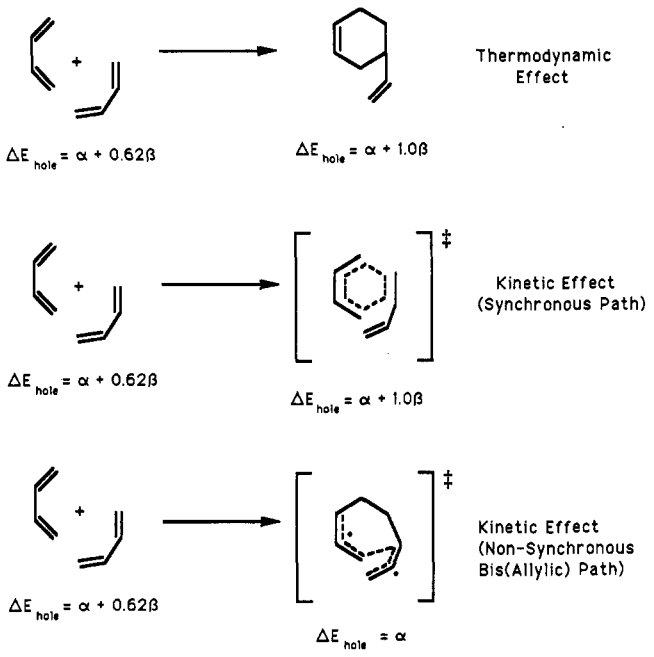
Scheme XIV



Synthetic Applications of the Diene/Electron-Rich Alkene Cycloaddition. The CB periselectivity of these reactions obviously provides valuable regiospecific and stereospecific synthetic access to 2-alkenylcyclobutyl ethers, sulfides, and amides. In addition, indirect but nevertheless efficient access to net Diels–Alder addition products is still available via a vinylcyclobutane rearrangement strategy.[15] This approach is illustrated for vinyl ethers in Scheme XII. The recognition of enamides as outstanding caticophiles has more recently made possible further important advances in this strategy (Schemes XIII and XIV).[16] The enamide/diene cycloaddition–hydrolysis–aminyl anion/vinylcyclobutane rearrangement sequence is especially attractive in that it permits efficient, net, intermolecular Diels–Alder addition to this normally quite recalcitrant type of dienophile. The caticophilicity of the enamide is so extraordinary that approximately stoichiometric proportions of enamide (1.2:1 enamide/diene) are employed in the cycloadditions. Concentrations of 1–2 M (PET conditions) make execution of the reactions on a 5–10-g (or larger) scale quite convenient. The reactions are, of course, completely CB periselective as well as (100%) regiospecific and stereospecific. Chemoselection is, usually, also exclusive or at least quite high, but syn/anti stereospecificity is minimal.

The Aminyl Anion/Vinylcyclobutane Rearrangement. The sequel to the cycloaddition (subsequent to basic hydrolysis) is the aminyl anion/vinyl-

Scheme XV

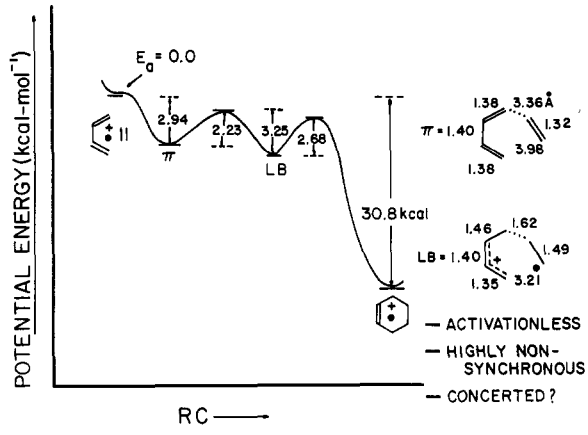


cyclobutane rearrangement. Although previously unknown, this reaction is essentially quantitative in each case. Equally impressively, rearrangement to a fully (di)substituted alkene terminus (Scheme XIV) reveals the extraordinary driving force of the reaction. The stereochemistry of the rearrangement is currently being investigated. The reaction sequence makes possible Diels–Alder additions to terminally Z-substituted and sterically hindered dienes which would not serve as dienic components even toward highly electron deficient neutral dienophiles.

Theoretical Basis for the Kinetic Impetus of Catical Cycloadditions. Catical cycloadditions are exceptional among cycloadditions in that they are facile enough to be incorporated into a radical type chain process as one of the propagation steps. Such propagation steps would normally be expected to have activation enthalpies of 0–5 kcal. Other than carbene additions, it is obvious that few neutral cycloadditions could meet this qualification. Theoretical studies of various types (FMO, MINDO/3, ab initio) have attempted to define the factors which provide such major kinetic impetus.[5,14,17,18] A simple FMO analysis (Scheme XV) is instructive.[14] The relative activation energy for the catical vs neutral Diels–Alder cyclodimerization of 1,3-butadiene is calculated from the energy of ionization of the pericyclic transition state relative to that of one of the reactant diene molecules. HMO energy levels are invoked, and both synchronous and nonsynchronous transition states are considered. The delocalized pericyclic array in the transition state for the synchronous path is benzene-like ($\Delta E_{hole} = \alpha + \beta$) and less caticogenic (more difficultly ionizable) than the reactant diene ($\Delta E_{hole} = \alpha + 0.62\beta$), revealing a negative kinetic impetus for this path. However, the bis(allylic)-like array of the transition state for the nonsynchronous path is much more caticogenic ($E = \alpha$) than the reactant diene. Consequently, a strong kinetic impetus is suggested and this path is expected to be strongly preferred. The stereospecificity observed

(18) Bellville, D. J.; Bauld, N. L. *Tetrahedron* **1986**, *42*, 6167.

Scheme XVI



experimentally for the catical Diels–Alder suggests an appropriate transition state model as being highly nonsynchronous but effectively (albeit weakly) concerted.

Buttressing relative transition state/neutral caticogenicity, theoretical studies also suggest that diminished nonbonded repulsions between a cation radical carbon site and a neutral carbon site render π-complex formation and covalent (including long bond) bond formation much more favorable than in the strictly neutral case.[14,17,18]

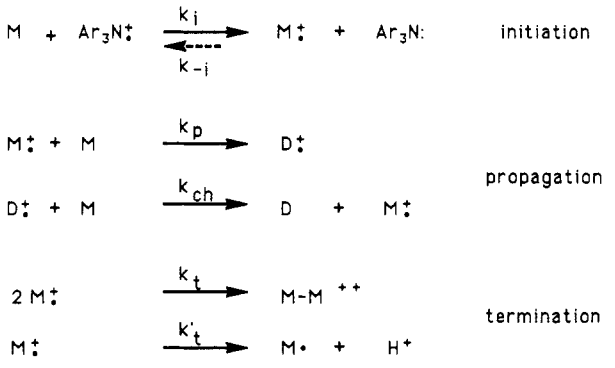
An extended basis set (6-31G//3-21G) ab initio SCF MO reaction path calculation for the (role-reversed) DA cycloaddition of the *s-cis*-1,3-butadiene catical to ethene (Scheme XVI) is in basic accord with these predictions.[18] First, the reaction is effectively *activationless* in the gas phase! The formation of a loose π complex ($E = -2.9$ relative to reactants; R_{45} and $R_{16} = 3.36$ and 3.98 Å, respectively) is predicted, the conversion of which to an intermediate requires only 2.23 kcal of activation. The intermediate (−4.0 kcal) is termed a "long-bond complex" because R_{45} (the initial bond being formed) is 1.62 Å. The subsequent closure of the 1,6 bond then requires only 2.7 kcal of activation. With a still better basis set (6-31G*//3-21G) this minimum completely disappears, indicating a concerted reaction.[19] This conclusion is further fortified by MP2 and MP3/6-31G*//3-21G calculations.

Kinetic Studies. Rigorous kinetic studies of the aminium salt initiated catical cyclodimerization of **2** and also of *trans*-anethole (**17**) have recently been completed.[20] The rate law for the cyclodimerization of **2**, for example, is rate = $k_{app}[Ar_3N^{\bullet+}]^{1/2}[2]^{3/2}$, a typical rate law for radical chain processes (half order in the initiating system consisting of $Ar_3N^{\bullet+}$ and **2** and first order in the monomer) which is exactly that predicted from a steady-state treatment of the proposed mechanism (Scheme XVII), with termination by coupling of two [$2^{\bullet+}$] caticals. The temperature dependence studies define apparent activation enthalpies ($\Delta H_{app}^{\ddagger}$) of 7.95 and 2.14 kcal/mol for the respective cyclodimerizations and activation entropies ($\Delta S_{app}^{\ddagger}$) of −26.9 and −29.8 eu. Cyclic voltammetric measurements of the half-wave oxidation potentials of **2**, **17**, and the neutral triarylamine **3** (1.60, 1.11, and 1.05 V vs SCE in dichloromethane, respectively) permit estimation of the activation enthalpies of the pericyclic step in each of these

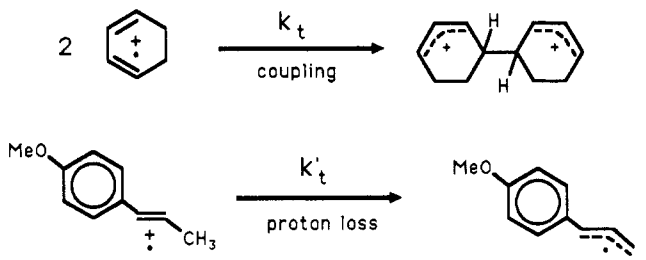
(19) Bauld, N. L., unpublished work.
(20) Bauld, N. L.; Lorenz, K. T. *J. Am. Chem. Soc.*, in press.

Scheme XVII

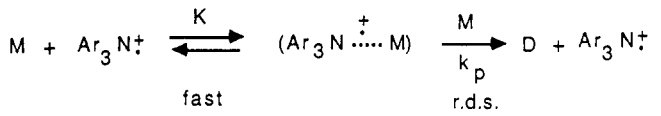
Cation Radical Chain Cyclodimerization



Chain Termination Steps



Scheme XVIII



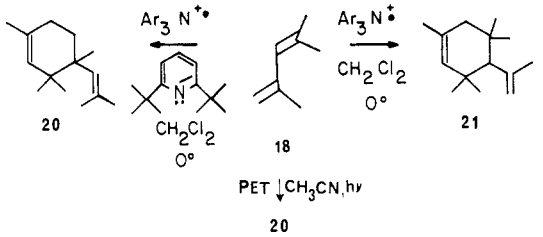
cyclodimerizations ($\Delta H_p^{\ddagger}$ = 1.6 and 0.8 kcal, respectively). These measurements clearly confirm the amazing kinetic impetus of catical cycloadditions (catalytic factors of ca. 10^{23} and 10^{49} are estimated) and are in good agreement with the theoretical results.

The Hypothetical "Complex" Mechanism. The rate law observed for the cyclodimerization of **2**, incidentally, decisively negates a hypothetical "complex mechanism" (Scheme XVIII) which would circumvent catical formation. This reaction mechanism corresponds to a rate law first order in aminium salt and second order in **2**. The complex mechanism is also decisively negated by the observation of strong rate retardation by added neutral triarylamine. In the catical chain mechanism, reversal of initiation and interception of catical chain intermediates is engendered by neutral triarylamine (**3**), but the complex mechanisms should be unaffected. A rate-determining formation of the hypothetical complex is also clearly excluded by the rate law.

Catical Chain vs Brønsted Acid Catalyzed Cycloadditions. One of the numerous aminium salt catalyzed cycloadditions reported by this group, viz., the cyclodimerization of 2,4-dimethyl-1,3-pentadiene (**18**),[6] has subsequently been found to occur via a Brønsted acid catalyzed mechanism (Scheme XIX).[21] This contention is strongly supported by the observation that the PET-initiated reaction yields a different Diels–Alder cyclodimer and that an added hindered

(21) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 7993.

Scheme XIX

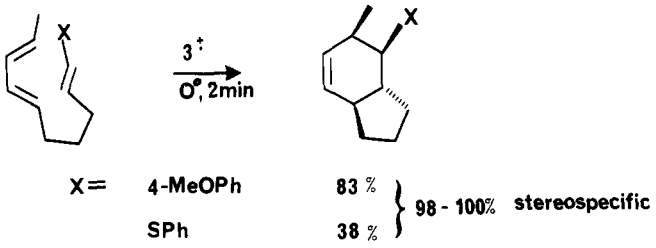


base (2,6-di-*tert*-butylpyridine, **19**) suppresses the formation of the former dimer and permits formation of the latter (PET) dimer under aminium salt conditions. These studies have helped focus attention on the distinction between catical and carbocation mechanisms, and in particular, the hindered base criterion has proved valuable in solidifying the mechanistic assignments previously made by this group. It is pertinent, first, to note that the synthetic utility of the unmodified aminium salt cyclodimerization of **2** is undiminished and, second, that since the catical cyclodimerization of **2** is still readily accessible by either the PET or hindered base-modified aminium salt procedure, the scope of catical chain cycloadditions has not diminished at all. Most important, of all the remaining (numerous) catical cycloadditions reported by this group either prior to or subsequent to the report of Brønsted acid catalysis, a thorough mechanistic scrutiny reveals no further examples of significant Brønsted acid catalysis. It should be noted that no question exists or has ever existed concerning the catical mechanism of the cyclodimerization of **2**, which is now decisively supported by detailed kinetic studies. The same, of course, can be said for the cyclodimerization of **17**. In the first paper of this group's series on catical cycloaddition,[5] further, a stereochemical observation was reported which decisively rules out a carbocation mechanism for the cross-addition of the 2,4-hexadienes (**9**) to **2** (and also, presumably, analogous cross-additions to **2**). The cycloadditions of all three geometric isomers of 2,4-hexadiene yield Diels–Alder adducts which not only reflect suprafacially stereospecific addition to the dienophilic double bond but which also, in every case, retain the original stereochemistry in the pendant propenyl group (Scheme VI). Protonation of **9**, of course, immediately eliminates this element of stereochemistry, even if one could somehow rationalize the exclusive reaction of the resulting unsymmetrically substituted allylic cation at a single terminus and then the subsequent rigorously stereospecific addition (both of which we consider unlikely).

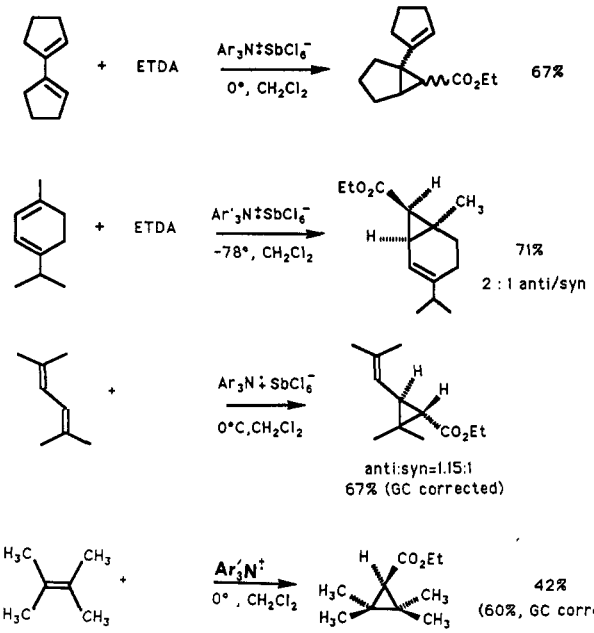
Nevertheless, the entire inventory of reactions was reexamined intensively by using a variety of criteria.[22] The response of the majority of the reactions to added hindered base is an increased yield of the same cycloadducts in approximately the same proportions (but note that a relatively large amount of catalyst must be used). For example, the yield of cyclodimers of **4** increases from 50% to 71%; the yield from **17** increases from 40% to 70%, and that from **11** increases from 1% to 17%. In no instance, other than **18**, is cyclodimerization completely suppressed, and in only one case is it even diminished (**2** + **6**). The catical nature

(22) Reynolds, Dan W.; Lorenz, K. T.; Chiou, H.-S.; Bellville, D. J.; Pabon, R. A.; Bauld, N. L., submitted for publication in *J. Am. Chem. Soc.*

Scheme XX



Scheme XXI



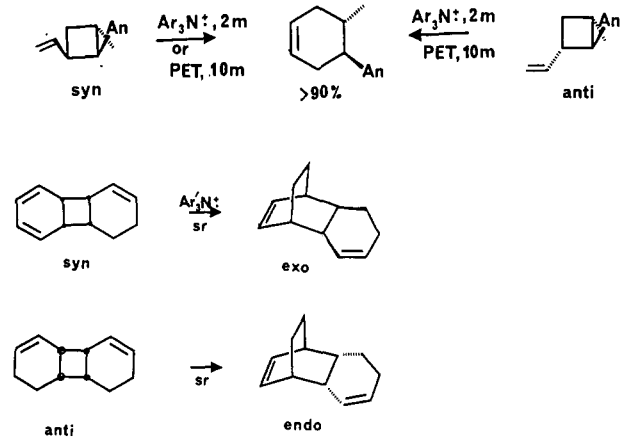
of this latter reaction is further confirmed by the finding of a large kinetic effect (rate retardation by added **3**; this is not observed for the cyclodimerization of **18**) and the failure of triflic acid/dichloromethane to effect any cross-cycloaddition between these two components under conditions where the cross-adducts are demonstrably stable, the reactants are decomposed, and **18** is smoothly cyclodimerized. A detailed GC/MS comparison of the products of the PET and aminium salt initiated reactions has also been carried out for this inventory and exact correspondence of products and even (approximately) product ratios confirmed (cf. previous comments about two reactions which do not proceed under PET conditions).

In summary, in the fairly lengthy inventory of catical cycloadditions studied in this laboratory, only one reaction (the aminium salt initiated cyclodimerization of **18**) appears to be Brønsted acid catalyzed. Even with this diene, the true catical cyclodimerization exists and is very efficient.

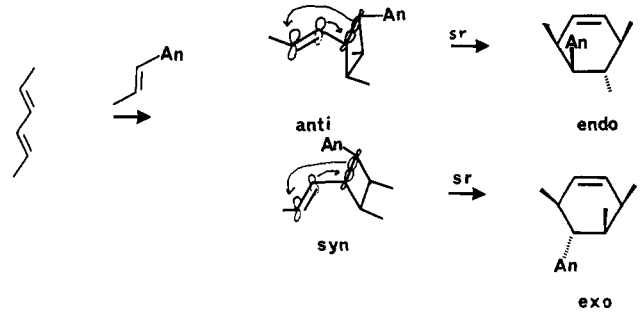
Intramolecular Catical Diels–Alder Cycloadditions. The special (entropic) driving force associated with intramolecular cycloadditions should be exciting to harness to the catical Diels–Alder, with its tremendous kinetic impetus. Research here is still at an early stage, but clear evidence is now available (Scheme XX) that such reactions are feasible and that the unusual endo selectivity of the catical Diels–Alder can be exploited to effect highly stereoselective ring juncture formation.[23]

(23) Harirchian, B.; Bauld, N. L. *Tetrahedron Lett.*, in press.

Scheme XXII



Scheme XXIII

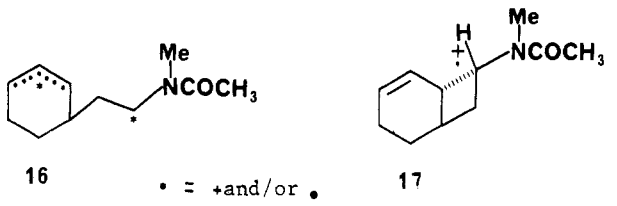


Catical Cyclopropanation. Recent research here has established that not only cyclobutanation and cyclohexenation but also cyclopropanation can be achieved by an aminium salt initiated catical chain mechanism (Scheme XXI).[24] Diene and styrene-type caticogens smoothly add to ethyl diazoacetate (ETDA) to effect cyclopropanation. Impressive chemoselection is also observed in cyclopropanation of unsymmetrical dienes. Even tetrasubstituted alkenes and halogenated dienes are smoothly cyclopropanated when a more powerful aminium salt initiator (tris(2,4-dibromophenyl)aminium hexachloroantimonate) is used.

Catical Sigmatropic Shifts. The catical Cope reaction has previously been exemplified by this group.[25] More recently, intramolecular 1,3 sigmatropic shifts in the form of catical vinylcyclobutane rearrangements have been found (Scheme XXII) to be quite efficient and sr stereospecific. In each case, retrocyclobutanation–Diels–Alder addition has been rigorously excluded.[26] This also provides, besides the direct catical Diels–Alder, an all-catical *indirect Diels–Alder* reaction involving cyclobutanation/1,3 shift. This mechanism has now been established in the catical addition of **17** to **9** (Scheme XXIII; contrary to our previous assumption of a direct catical DA[27]). More-

(24) Stufflebeme, G.; Lorenz, K. T.; Bauld, N. L. *J. Am. Chem. Soc.* **1986**, *108*, 4234.
(25) Lorenz, K. T.; Bauld, N. L. *J. Catal.* **1985**, *95*, 613.
(26) Bauld, N. L.; Reynolds, D. W.; Harirchian, B.; Marsh, B. K.; Chiou, H.-S., submitted for publication in *J. Am. Chem. Soc.*
(27) Reynolds, D. W.; Bauld, N. L. *Tetrahedron* **1986**, *42*, 6189.

Scheme XXIV



over, the indirect mechanism may compete with the direct mechanism in DA cycloadditions where the dienic component is acyclic.[28] The catical Diels–Alder cyclodimerization of **2**, however, occurs exclusively via the direct route, since the cyclobutane cyclodimers are stable under the usual [tris(4-bromophenyl)]aminium salt conditions.[26]

Initiator Systems. Although the aminium salt and PET initiator systems appear to be preferred for laboratory synthetic purposes, a variety of other systems have been or are being developed. These include catical polymers,[29] zeolites,[25,30] and electrochemical oxidation.[31]

(28) Chiou, H.-S., The University of Texas at Austin, unpublished research.

Zeolites in particular have been used to catalyze both cycloadditions and 1,5 shifts. Catical cycloadditions have also been observed on doped montmorillonite clays.[32]

Conclusion. Five distinct types of catical pericyclic reactions have now been exemplified. These are (1) cyclobutanation, (2) Diels–Alder addition, (3) cyclopropanation, (4) Cope rearrangement, and (5) [1,3] sigmatropic shifts (vinylcyclobutane rearrangements). Most of these reactions have a substantial range of synthetic utility, as well as unusually good selectivity. The emergence of catical chain reactions as a viable and significant catalytic principle therefore appears to be decisively documented. The catical function has been described as a new and highly reactive functional group. It is also more than that; in a valid sense it is a universal functional group since, potentially, any neutral function (or even nonfunction) can be transformed by a fundamental ionization process to its corresponding catical function.

We thank the NSF (CHE-8521671), NIH (GM 34281), and Welch (F-149) for support of this research.

(29) Bauld, N. L.; Bellville, D. J.; Gardner, S. A.; Migron, Y.; Cogswell, G. *Tetrahedron Lett.* **1982**, *23*, 825.
(30) Ghosh, D.; Bauld, N. L. *J. Catal.* **1985**, *95*, 300.
(31) Mecock, J.; Steckhan, E. *Tetrahedron Lett.* **1987**, *28*, 1081.
(32) Laszlo, P.; Lucchetti, J. *Tetrahedron Lett.* **1984**, *25*, 1567.