Cation Radical Catalyzed Diels–Alder Reaction of Electron-Rich Allenes†

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The cation radical catalyzed cycloaddition of electron-rich arylallenes **1a–e** with 1,2,3,4,5-pentamethylcyclopentadiene (**2a**) afforded the Diels–Alder products **3** and **4** at 0 °C in 5 min with a high chemoselectivity, facial selectivity, and stereoselectivity. From the results of various mechanistic tests, it is inferred that the electron transfer induced reaction proceeds via a [3 + 2] pathway by cycloaddition of the diene cation radical to a neutral allene **1** exhibiting a rather short chain length. However, with electron-withdrawing substituents at the remote end of the allene functionality, the cycloaddition is only a minor reaction path. With diarylallene **1f** and diene **2a** or **2b**, no cycloaddition but formation of products **7** and d_1-**7** occurred. It is concluded that distonic cation radicals may be intermediates in a stepwise formal Diels–Alder reaction induced by electron transfer.

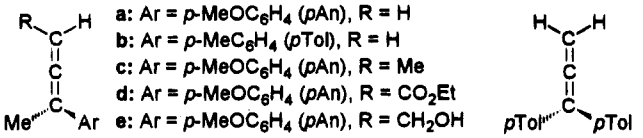
Introduction

Diels–Alder (DA) cycloadditions with allenes as dienophiles provide a valuable approach to cyclic systems with a reactive *exo*-alkylidene moiety, which is advantageous for further transformations often required in the synthesis of natural products.[1] Unfortunately, allene cycloadditions are often hampered by a low periselectivity allowing the [2 + 2] cycloaddition to successfully compete with the DA reaction.[2] In addition, the classical variant of this reaction which is usually conducted under thermal conditions is restricted in its scope by the necessity of an appropriate HOMO–LUMO interaction of the reactants as rationalized in terms of the FMO theory.[3] This requirement for a donor–acceptor complementary is fulfilled in the normal DA cycloaddition of electron-deficient allenes with electron-rich dienes[4] and vice versa in the inverse reaction of electron-rich allenes with electron-deficient dienes.[5] In contrast, [4 + 2] cycloadditions of both electron-rich allenes and dienes have only been feasible by activating either reactant, e.g., by generating a carbocation adjacent to the allene moiety.[6]

An alternative approach to accelerate cycloadditions, the cation radical catalyzed DA cycloaddition, has been elaborated during the past decade, constituting an interesting synthetic methodology.[7] By adding catalytic amounts of one-electron oxidants, the activation energy of the cycloaddition may be extremely reduced, leading to impressive rate accelerations at mild reaction conditions.[7,8] Our successful application of this methodology to the cation radical catalyzed DA cycloaddition of arylmethylketenes[9] suggested that one-electron oxidation may be a viable strategy as well to initiate the [4 + 2] cycloaddition of electron-rich allenes as dienophiles with dienes. The first examples of this hitherto unknown reaction[10] were recently described in a preliminary communication.[11] Some more examples, in particular the influence of allene and diene structure, and a detailed mechanistic investigation constitute the content of this paper leading to a critical assessment of the scope of this new reaction mode.

Results

Allenes **1a–d** and **1f** were prepared as described in the literature, while **1e** was obtained from reduction of **1d** by diisobutylaluminum hydride in benzene. When solutions of allenes **1a–c** and **1f** and diene **2a** in toluene were heated to reflux for several days, only for the system **1b/2a** were DA products (2%) observed. Moreover, with



1a-1e **1f**

increasing reaction time, in all cases significant amounts of polymers resulted. Similarly, we were unsuccessful in triggering the DA cycloaddition of **1a/2a** in the presence of Lewis acids such as BF_3·OEt_2 and $AlCl_3$. In

† Electron Transfer Catalyzed Reactions. 6. For part 5, see ref 12.

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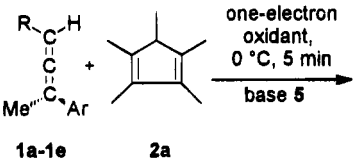
Table 1. Electron Transfer Initiated Cycloadditions of Allenes 1a–f and Diene 2a (E_{pa} = 0.54 V)[a] with ET1 under Standard Conditions (1/2a/ET1 = 5/1/1)[b]

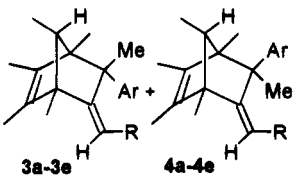
			yield (%)		
allene 1	E_{pa} [V][a]	5[c]	3	4	further products
1a	0.94	+	67	13	
1a	0.94	–	31	6	43 (**6a**)
1b[d]	1.23	+	48	12	
1b[d]	1.23	–	6	1	9 (**6b**)[e]
1c	0.93	+	63	9	
1c	0.93	–	43	9	dimers of **1c**
1d	1.11	+	4	1	
1d	1.11	–	10	1	10 (*E*-**9**); 1 (*Z*-**9**)
1e	0.95	+	68[f]	13[f]	
1e	0.95	–			dimers of **1e**
1f[d]	1.07	+			13 (**7**)
1f[d]	1.07	–			11 (**7**); 30 (**8**)

[a] Anodic peak potential vs Fc/Fc$^{+\bullet}$. [b] Reaction at 0 °C, within 5 min in acetonitrile. Analysis by ^{1}H NMR. Yields based on **2a**. [c] >100 mol % related to initiator. [d] In acetonitrile:methylene chloride = 1:1. [e] +7% of a further isomer, probably the *exo*-isomer of **6b**. [f] Yield based on isolated product.

contrast, norbornenes **3a–e** and **4a–e** were obtained smoothly at 0 °C from the cation radical initiated cycloaddition of allenes **1a–e** with diene **2a**, as long as acid-catalyzed processes, which are simultaneously triggered by the one-electron oxidation, were suppressed by addition of 2,6-di-*tert*-butylpyridine (**5**) as base (eq 1). No [2 + 2] cross cycloadduct could be detected within the limits of our analytical methods.



1a-1e **2a**



3a-3e **4a-4e** (1)

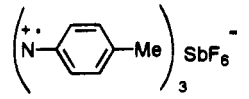
In general, a suspension of the one-electron oxidant (Chart 1) was added to a solution of allene **1**, diene **2a**, and base **5** within 2 min. After 5 min the reaction was quenched by addition of a sodium methoxide solution in methanol, and after workup the DA products were afforded in good yields (Table 1). A more detailed analysis of the yield of DA products as a function of the various reaction parameters was obtained for the systems **1a–c/2a** (see Tables 2–4).

In addition, the nortricyclanes **6a,b** were formed as byproducts when the corresponding cycloadditions were conducted in the absence of base **5**. From the cation radical initiated reaction of allene **1f** and dienes **2a** and **2b** resulted no DA products but the adducts **7** and **8**.

All products were isolated through liquid chromatography and purified through HPLC. Unequivocal identification of all compounds was achieved by IR, MS, ^{1}H NMR, ^{13}C NMR, and ^{1}H NMR difference NOE spectra. The mass spectra of all norbornenes showed strong signals derived from a [4 + 2] cycloreversion and no further intense signals.

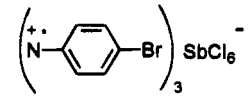
The detailed stereochemical relationships within **3c**

Chart 1. One-Electron Oxidants Used in This Study and Their Redox Potentials vs Fc/Fc$^{+\bullet}$



ET1

$E_{1/2}$ = 0.37 V



ET2

$E_{1/2}$ = 0.70 V

Fe(4,7-(OMe)$_2$phen)$_3$(PF$_6$)$_3$

ET3

$E_{1/2}$ = 0.38 V

Fe(phen)$_3$(PF$_6$)$_3$

ET4

$E_{1/2}$ = 0.69 V

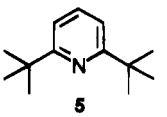


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Table 2. Detailed Results of the Electron Transfer Initiated Cycloaddition Reaction of 1a with 2a[a]

					yield [%]		
entry	ratio 1a:2a	initiator	mol % of oxidant	base 5[b]	3a	4a	6a
1	1:1	**ET1**	25	+	10	2	
2	1:1	**ET1**	100	+	54	10	
3	3:1	**ET1**	25	+	25	5	
4	3:1	**ET1**	100	+	58	10	
5	3:1	**ET1**	100	–	31	6	43
6	3:1	**ET4**	25	+			
7	3:1	**ET4**	25	–	7		14
8	3:1	**ET3**	50	+			
9	3:1	**ET3**	50	–	38	8	
10	5:1	**ET1**	25	+	30	6	
11	5:1	**ET1**[c]	25	+	46	8	
12	5:1	**ET1**	100	+	67	13	
13	5:1	**ET2**	25	+	11		

[a] Reaction at 0 °C, within 5 min in acetonitrile. Analysis by ^{1}H NMR. Yields based on **2a**. [b] >100 mol % related to initiator. In presence of 500 mol % tris(4-methylphenyl)amine related to **ET1**.

Table 3. Electron Transfer Initiated Cycloadditions of 1b and 2a in the Presence of ET1[a]

				yield [%]		
ratio 1b:2a	solvent ratio CH_3CN:CH_2Cl_2	mol % of **ET1**	base 5[b]	3b	4b	6b
5:1	CH_2Cl_2	100	+	34	7	
5:1	CH_2Cl_2	100	+	24	5	
5:1	CH_2Cl_2	100	+	24	5	
5:1	1:1	100	+	48	12	
5:1	1:1	100	+	45	11	
5:1	2:1	100	+	31	6	
5:1	1:1	100	–	6	1	9[c]
5:1	1:1	25	+	20	5	
1:1	1:1	25	+	7	2	

[a] Reaction at 0 °C, within 5 min. Analysis by ^{1}H NMR. Yields based on **2a**. [b] >100 mol % related to initiator. [c] 7% of a further isomer, probably the *exo*-isomer of **6b**.

could be deduced from positive NOE effects (Chart 2) between (1) aryl protons and methyl protons 11-H and 12-H (*endo*-isomer), (2) proton 7-H and methyl group 9-H (*anti*-isomer), (3) proton 14-H and methyl group 8-H (*Z*-isomer), and (4) methyl group 15-H and aryl protons (*Z*-

(10) So far, only allene cycloadditions triggered by photoinduced electron transfer have been described: (a) Haddaway, K.; Somekawa, K.; Fleming, P.; Tossell, J. A.; Mariano, P. S. *J. Org. Chem.* **1987**, *52*, 4239–4253. (b) Maruyama, K.; Imahori, H. *J. Org. Chem.* **1989**, *54*, 2692–2702.

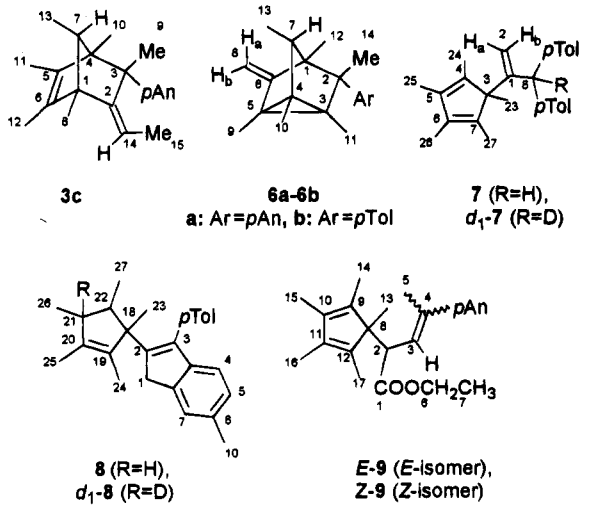
(11) Schmittel, M.; Wöhrle, C. *Tetrahedron Lett.* **1993**, *34*, 52, 8431–8434.

Table 4. Electron Transfer Initiated Cycloadditions of 1c and 2a in the Presence of ET1[a]

entry	ratio 1c:2a	mol % of ET1	5[b]	yield [%] 3c	yield [%] 4c
1	5:1	100	+	63	9
2	5:1	100	–	43	9[c]
3	5:1	25	+	44	11
4	1:1	100	+	43	7

[a] Reaction at 0 °C, within 5 min in acetonitrile. Analysis by ^{1}H NMR. Yields based on **2a**. [b] >100 mol % related to initiator. [c] Further products, probably dimers of **1c**.

Chart 2



isomer). Besides, the methyl group 11-H is shifted to a higher field (δ = 0.57 ppm) in the ^{1}H NMR which may only be explained by the presence of an *endo*-anisyl group, whereas the signal of the methyl group 12-H is located at δ 1.46 ppm. The high-field shift of methyl protons 13-H (δ 0.68 ppm) and the above NOE effects support the *anti* assignment of **3c**. In addition, we observed coalescence of the aryl signals in the ^{1}H and ^{13}C NMR spectra, because rotation of the anisyl ring is hindered by the 15-H methyl group. In light of the importance of the stereochemical assignments the structure of **3c** was additionally confirmed by X-ray analysis.[12]

The *exo* structure of **4c** is confirmed by the absence of a high-field shift for methyl group 11-H (δ 1.48 ppm) together with absence of coalescence for aryl protons in the ^{1}H and ^{13}C NMR spectra. Moreover, NMR data of the *exo*-isomer **4c** are fully in accordance with those for the correspondingly substituted norborn-5-en-2-one.[9] As NMR data of the remaining norbornenes closely resemble those of **3c** and **4c**, their stereochemistry and structure were inferred by analogy.

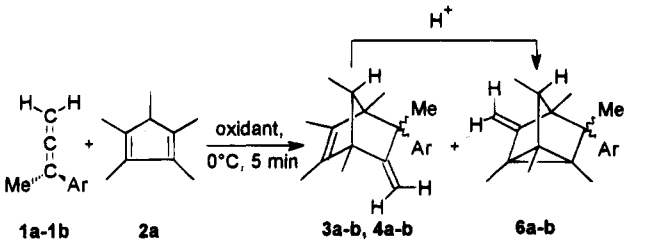
In contrast to the corresponding norbornenes **3a** and **3b**, the mass spectra of nortricyclanes **6a** and **6b** display only negligible fragmentation induced by cycloreversion. Furthermore, NOE enhancements (between 8-H_a and 12-H, 13-H; between 8-H_b and 9-H) as well as ^{1}H and ^{13}C NMR shifts[13] strongly confirm the position of the exocyclic double bond and the *anti,endo* configuration of **6a** and **6b**.

NMR spectra of alkene **7** establish the symmetric structure containing a methylene group, the position of which was assigned by characteristic NOE effects. Characteristically, in the mass spectrum only fragmentation to diene **2a** but not to allene **1f** was found.

Discussion

The present results demonstrate the potency of electron transfer initiation to accomplish under mild conditions Diels–Alder reactions which can be triggered neither by thermal activation nor by Lewis acid catalysis. Hence, for the first time electron-rich allenes could be reacted as dienophiles with an electron-rich diene, i.e., **2a**, in yields up to 81% (Table 1). The reaction conditions are similar to the ones in the DA reaction of **2a** and ketenes induced by aminium salts.[9] Consequently, in order to better understand the reaction mode and to use the one-electron oxidation strategy more efficiently, several questions related to the mechanism of this DA reaction needed to be answered.

Acid vs Electron Transfer Catalysis. Since proton-catalyzed processes are often readily triggered under one-electron oxidation conditions in light of the high acidity of cation radicals, it is important to differentiate between electron transfer and acid-induced processes.[6] For our examples, however, an acid catalysis could definitely be ruled out, since all DA products **3**–**4** were formed even in the presence of a slight excess of 2,6-di-*tert*-butylpyridine (**5**). Furthermore, in all cases, except for allene **1d** (which will be discussed later), removal of base **5** entailed a yield decrease in the DA products (Table 1). Rather other products were increasingly formed in the absence of **5**, e.g., nortricyclanes **6a** and **6b** as well as dimers of the allenes. Since **6a** and **6b**, respectively, could be afforded from the slow rearrangement of **3a** or **3b** in $CDCl_3$ indicating a proton-catalyzed process, we assume that they are formed by acid catalysis during the DA reaction as well (eq 2).



a: Ar = *p*An; **b**: Ar = *p*Tol. (2)

Hence, acid induced side reactions, if admitted through the choice of the reaction conditions, do restrain or in one case (**1e** and **2a**) even totally impede formation of products **3** and **4**, indicating that the latter are indeed produced by an electron transfer route. Moreover, since the cycloaddition of **1a** and **2a** was successfully initiated either by outer-sphere oxidants (the iron(III)phenanthrolines **ET3** and **ET4**) and by the aminium salts **ET1** and **ET2** (inner-sphere oxidants), we suggest that free cation radicals are the reactive intermediates in this DA reaction and that complexes with aminium salts are not involved.[14] This mechanistic proposal is further corroborated by the finding that use of the weaker oxidant **ET1** leads to higher product yields than **ET2** (Table 2),

(12) Keller, M.; von Seggern, H.; Schmittel, M.; Wöhrle, C. *Z. Kristallogr.* **1995**, *210*, 602–604.
(13) Carnardi, H.; Giordano, C.; Heldeweg, R. F.; Hogeveen, H.; van Kruchten, E. M. G. A. *Isr. J. Chem.* **1981**, *21*, 227–238.
(14) The reduced yields with the **ET3, ET4** can readily be understood with the increased Coulomb repulsion in the reduction of the $DA^{+\bullet}$ by $Fe(phen)_3^{2+}$ as compared with reduction through the amine, see ref 9b.

because reduction of the product cation radical is apparently one of the pivotal steps in this reaction mode. Consequently, the yield can be increased through deliberate addition of the reduced one-electron oxidant (Table 2, entry 11) by accelerating the reduction of the product cation radical.

Diels–Alder Reaction: [3 + 2] vs [4 + 1] Mechanism. The question of a [3 + 2] or a [4 + 1] mechanism has been a debatable topic over the past decade for many cation radical catalyzed cycloadditions. A [4 + 1] mechanism has been favored for years, since in contrast to the [3 + 2] variant it is formally symmetry allowed[15] and in essence all of the earlier cation radical DA cross-reactions involved readily oxidizable dienophiles.[7] Only recently, the decisive studies by Steckhan,[16] Bauld,[17] and us[9b] have disclosed that the [3 + 2] pathway is a viable mechanistic choice, if the diene prefers the s-*cis* conformation.

From our results, the cation radical initiated allene/diene cycloaddition most likely follows the [3 + 2] pathway (eqs 3–5) and not the [4 + 1] pathway (eqs 6–8).

[3 + 2] mechanism

$$\text{diene} - e^- \rightarrow \text{diene}^{+\bullet} \quad (3)$$

$$\text{diene}^{+\bullet} + \text{allene} \rightarrow \text{DA}^{+\bullet} \quad (4)$$

$$\text{DA}^{+\bullet} + \text{diene (or } NR_3) \rightarrow \text{DA} + \text{diene}^{+\bullet} \text{ (or } NR_3{}^{+\bullet}) \quad (5)$$

[4 + 1] mechanism

$$\text{allene} - e^- \rightarrow \text{allene}^{+\bullet} \quad (6)$$

$$\text{allene}^{+\bullet} + \text{diene} \rightarrow \text{DA}^{+\bullet} \quad (7)$$

$$\text{DA}^{+\bullet} + \text{allene (or } NR_3) \rightarrow \text{DA} + \text{allene}^{+\bullet} \text{ (or } NR_3{}^{+\bullet}) \quad (8)$$

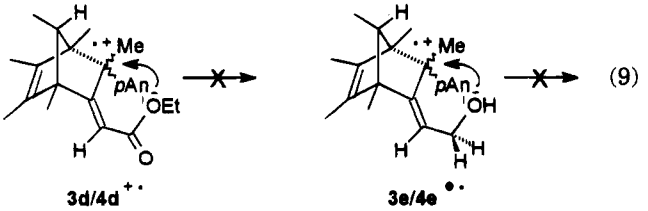
This role selectivity can easily be understood from the results of various mechanistic tests in Tables 1–4. Two important arguments are in favor of a [3 + 2] cycloaddition[7,9,17] as opposed to the [4 + 1] mechanism: first, the oxidation potential of **2a** (E_{pa} = 0.54 V) is significantly lower than the ones of allenes **1** ($E_{pa} \geq$ 0.93 V, see Table 1); second, the product yield can be significantly improved by increasing the allene/diene ratio. Furthermore, control experiments indicate that allene **1a** for itself is oxidized only very slowly by **ET1**[18] while in the reaction of **2a** with **ET1** dimers and dehydrodimers of **2a** are formed readily.[9]

Accordingly, the cycloaddition starts by generation of the diene cation radical that is trapped by allene **1** to yield the DA cation radicals of $\mathbf{3}^{+\bullet}/\mathbf{4}^{+\bullet}$, which are finally reduced either by the diene **2a** or the reduced initiator. Hence, increasing the allene to diene ratio up to **1:2a** = 5:1 leads to better product yields, because trapping of a diene cation radical with an allene is accelerated. One reason for the failure of the [4 + 1] format is presumably the rapid deprotonation of the allene cation radicals.[10,19] In fast scan cyclic voltammetry studies allenes **1a–f** showed irreversible waves even at scan rates up to $v = 5 \times 10^4$ V s^{-1}.

Due to unidentified side pathways, some of which most likely constitute deprotonation reactions, e.g., of the primarily formed diene cation radical, best product yields were obtained at a ratio oxidant to diene = 1:1. Nevertheless, entries 3, 10, and 11 in Table 2 indicate that the cycloaddition is catalytic in nature, but with a rather short chain length. The high amount of oxidant needed is therefore rationalized by formation of readily oxidizable radicals resulting from the deprotonation of intermediate cation radicals. Oxidation of these radicals followed by the deprotonation of the resulting cations should lead to unsaturated compounds again prone to oxidation. Hence, several oxidation equivalents are thought to disappear in a low-yield side product accounting for the large amount of oxidant needed.

Substituent Effects. As shown in Table 1, the introduction of a substituent at the not-involved cumulene double bond of allene **1a** may significantly influence the amount of DA adducts. For example, when using the same reaction conditions for the cycloaddition of **1a/2a** and **1d/2a** the yield in the corresponding DA products dropped from 80% to 5%. Apparently, electron-withdrawing substituents are not tolerated even at the remote end of the allene, which is not directly involved in the cycloaddition.

It is important to note that oxidation potential differences of the two reactants ($\Delta\Delta E_{pa}$), an argument quite often advanced in the recent literature,[16] cannot account for this effect since the yield in system **1b/2a** ($\Delta\Delta E_{pa}$ = 0.69 V) is much better (60%) than with **1d/2a** (5%) despite $\Delta\Delta E_{pa}$ = 0.57 V. Similarly, steric hindrance certainly does not play a decisive role because with the trisubstituted allenes **1c** and **1e** the yields in their reaction with **2a** (72% and 81%, respectively) were comparable to the reaction with **1a** (80%). Moreover, a plausible mechanistic explanation for the failure to obtain better yields with **1d/2a**, namely, that the intermediate DA cation radical $\mathbf{3d,4d}^{+\bullet}$ might be trapped by intramolecular nucleophilic attack,[11] can now be definitely be ruled out since one would expect this detrimental reaction mode to occur in $\mathbf{3e,4e}^{+\bullet}$ even more, but in that case good yields of the cycloadducts were observed (eq 9).

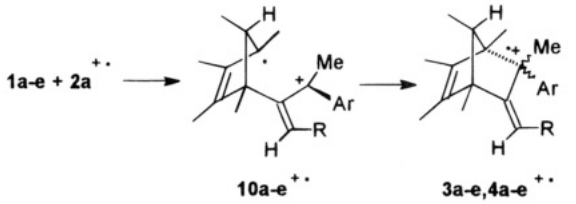


(9)

A plausible, but nevertheless speculative explanation for the low yield in the reaction **1d/2a** is provided by the surprising outcome of the cation radical reaction when carried out in the absence of base **5**. Unlike all other examples, the yield of **3d/4d** was increased in absence of **5**, indicating that deprotonation of an intermediate cation radical can compete with the cycloaddition route. If we

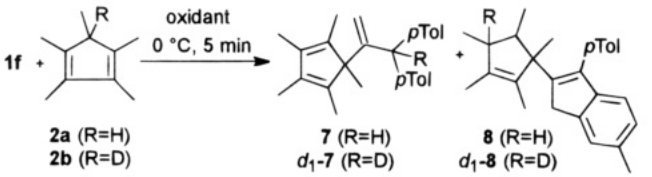
(15) Bauld, N. L.; Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378–2382.
(16) Mlcoch, J.; Steckhan, E. *Tetrahedron Lett.* **1987**, *28*, 1081–1084.
(17) Chokalingam, K.; Pinto, M.; Bauld, N. L. *J. Am. Chem. Soc.* **1990**, *112*, 447–448.
(18) When **ET1** was added to a solution of **1a** under DA conditions, the deep-blue initiator solution was not decolorized. Analysis by ^{1}H NMR and GC-MS showed, that the crude mixture only consisted of tristolylamine and allene **1a**.
(19) (a) Becker, J. Y.; Zinger, B. *Tetrahedron* **1982**, *38*, 1677–1682. (b) Becker, J. Y. *Isr. J. Chem.* **1985**, 26,196–206. (c) Klett, M. W.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 6615–6220.

Scheme 1



accept the assumption that $\mathbf{2a}^{+\bullet}$ adds to **1d** as rapid as to the other monoarylallenes based on anodic peak potential considerations, this may point to the occurrence of the distonic cation radical $\mathbf{10}^{+\bullet}$ as crucial intermediate, the acidity of which is particularly augmented by introduction of the electron-withdrawing ethoxy carbonyl group (R = CO_2 CH_2CH_3) (Scheme 1).

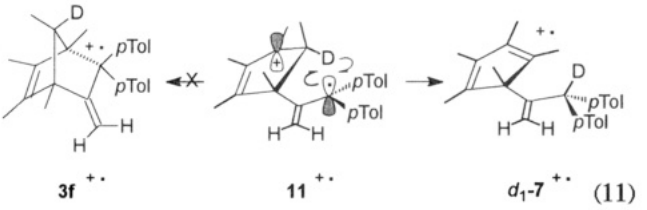
Variation of the aryl substituent at the cumulene double bond involved in the cycloaddition is possible. Hence, when the anisyl group of allene **1a** (E_{pa} = 0.94 V) is replaced by a tolyl group (**1b**, E_{pa} = 1.23 V), the yield of cycloadducts decreases from 80% to 60%. Presumably the cycloaddition is slightly retarded by increasing the gap between the oxidation potential of the allene and diene ($\Delta\Delta E_{pa}$).[16] In contrast, however, introduction of two tolyl groups as in **1f** (E_{pa} = 1.07 V) results in no cycloaddition at all, although the redox potential of the allene is lower and hence $\Delta\Delta E_{pa}$ is even better. The failure to form the closed structures of DA cation radical $\mathbf{3f}^{+\bullet}$ can be ascribed to steric hindrance. Even broad variation of the reaction conditions (addition of tritolylamine, addition of lithium perchlorate, reaction at −25 °C, presence of sodium carbonate) did not entail detectable amounts of DA cycloadducts, but instead the cross adducts **7** and **8** were afforded (eq 10). Importantly, formation of the latter product could be totally suppressed upon addition of base **5**, indicating that it is formed via acid catalysis.



(10)

To understand better the way **7** and **8** were formed, we examined the reaction of **1f** with the deuterated diene **2b**. In analogy, the deuterated products d_1-**7** and d_1-**8** were afforded, with product d_1-**8** certainly derived from an acid-catalyzed process involving proton addition to **2b** followed by addition of the resulting cation to **1f** and a Nazarov-type cyclization. In contrast, formation of d_1-**7** provides indirect evidence for an intermediate distonic cation radical, $\mathbf{11}^{+\bullet}$, that for steric reasons cannot close to the DA cation radical $\mathbf{3f}^{+\bullet}$. Rather, intramolecular[20] deuterium abstraction takes place to afford d_1-$\mathbf{7}^{+\bullet}$ which is finally reduced by electron transfer (eq 11).

Although our conclusion may only be tentative at present, the results with reactions **1d/2a** and **1f/2a** support the hypothesis that the cation radical catalyzed allene/diene cycloaddition is indeed a stepwise process, with the ring closure of the distonic cation radical $\mathbf{10}^{+\bullet}$



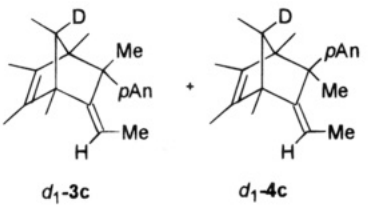
(11)

to the $DA^{+\bullet}$ being the critical step. One major problem in thermal cation radical chemistry, namely, generating the $DA^{+\bullet}$ from the distonic cation radical, is not as crucial a point in photoinduced electron transfer reactions, because back electron transfer can occur to the open distonic cation radical as well. Hence efforts in the near future will also be directed toward using PET initiation.

Selectivity. A straightforward analysis reveals that the cation radical catalyzed cycloaddition proceeds with a high degree of "DA periselectivity", since in no case could [2 + 2] cycloadducts be detected. Moreover, for each system (**1c–e/2a**) only two isomers out of 16 possible ones are formed, indicating a remarkable facial selectivity, chemoselectivity, and stereoselectivity. Steric hindrance in the approach of allene and diene cation radical in the cycloaddition step is certainly responsible for the exclusive *anti*-facial selectivity.[21] Moreover, the observed chemoselectivity for the more electron-rich, aryl-substituted double bond is due to the better stabilization of the intermediate DA cation radical. Furthermore, if there is a substituent located at the forming exocyclic double bond, steric interaction with the methyl group at the adjacent bridgehead only permits formation of *Z*-isomers. Only the differentiation of *endo* and *exo* transition states is less selective; the *endo*-isomers were formed favorably in all [4 + 2] cycloadditions, with *endo* to *exo* ratios ranging in between 4:1 and 6:1, in accordance with stereoselectivities observed in other cation radical catalyzed cycloadditions.[22]

Using our best conditions for the system **1b/2a/ET1** disclosed that the yield of **3b/4b** is slightly affected by solvent composition (Table 3). The best result (60%) was obtained at an acetonitrile to methylene chloride ratio of 1:1. In contrast to many reports in the literature, methylene chloride did not prove superior to acetonitrile. Rather the yield was augmented with increasing amounts of acetonitrile, but since allene **1b** is only sparingly soluble in acetonitrile, the cycloaddition could not be carried out in pure acetonitrile.

Other Dienes. Not surprisingly, the reaction of **1c** with **2b** provided the deuterated norbornenes d_1-**3c** and d_1-**4c**.



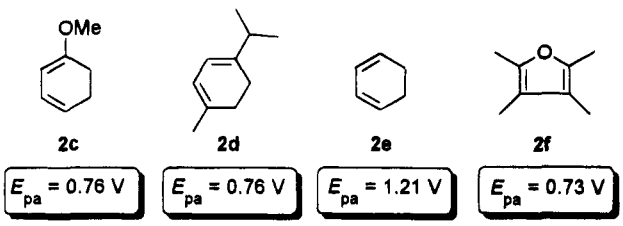
When, however, allenes **1a–f** were reacted with dienes **2c–f** (Chart 3) in the presence of oxidants **ET1** or **ET2**, analysis of the crude mixtures by ^{1}H NMR indicated

(20) As an alternative intermolecular hydrogen atom transfer from unoxidized d_1-**2a** could take place followed by deprotonation of the resulting cation.

(21) Burnell, D. J.; Valenta, Z. *J. Chem. Soc., Chem. Commun.* **1985**, 1247–1248.

(22) Lindsay, J. R.; Norman, R. O. C.; Stillings, M. R. *Tetrahedron* **1987**, *34*, 1381–1383.

Chart 3



neither DA cycloadducts nor other low-weight products in significant amounts.

The problems with using other dienes than **2a** and **2b** in the cycloaddition with allenes **1a–f** is reminiscent of our results with ketenes[9] but is hard to reconcile with findings of other cation radical catalyzed cycloadditions,[7,16] where dienes could be varied in a wide range. At the present moment, we suppose that allenes cannot be reacted via a [4 + 1] cycloaddition pathway; hence all dienes with higher oxidation potentials are not suited (e.g., **2e** with E_{pa} = 1.21 V). Some of the selected dienes, however, exhibited lower oxidation potentials than our model allenes, but still would not react. Apparently, with those cross cycloaddition can kinetically not compete with deprotonation of the diene cation radical and diene + diene$^{+\bullet}$ cycloaddition processes, but as long as rate data are missing this hypothesis is open for discussion.

In summary, we successfully extended the scope of allenes as dienophiles in DA reactions by electron transfer initiation. From the mechanistic results it is inferred that distonic cation radicals may play an important role as intermediates in the stepwise cycloaddition.

Experimental Section

General Methods. For instrumentation used in this work, see ref 9b. $CDCl_3$ was the solvent of choice for all NMR experiments unless noted otherwise. Cyclic voltammetry experiments were performed in homemade cells, consisting of a disk working electrode, an auxiliary electrode (platinum wire), and a Ag/AgCl reference electrode. For standard voltammetric experiments a platinum working electrode (diameter = 1 mm) was used and a 10^{-3} M solution of the substrate in acetonitrile or methylene chloride containing tetra-*n*-butylammonium hexafluorophosphate (0.1 M) was examined at a scan rate of 0.1 V s^{-1}. The voltage sweep was controlled by a Princeton Applied Research 362 potentiostat. All potentials were referenced to ferrocene as internal standard with $E_{1/2}$ = 0.390 V vs SCE.[23] The dienes **2a–e** and 2,6-di-*tert*-butylpyridine (**5**) were reagent grade materials, freshly distilled before use.

One-Electron Oxidants. ET1 was synthesized from commercially available tris(4-methylphenyl)amine (Kodak) and nitrosonium hexafluoroantimonate in acetonitrile. Commercial **ET2** was used after extensive rinsing with dry ether. Tris(1,10-phenanthroline)iron(III) hexafluorophosphate (**ET4**) and tris(4,7-dimethoxy-1,10-phenanthroline)iron(III) hexafluorophosphate (**ET3**) were prepared according to the literature by oxidation of the corresponding iron(II) phenanthrolines.[24]

Allenes 1a–f. Allenes **1a** and **1b** were prepared from the corresponding substituted acetophenones following literature procedures.[25,26]

1,3-Dimethyl-1-(4-methoxyphenyl)allene (1c). To a solution of (*E,Z*)-2,3-dimethyl-2-(4-methoxyphenyl)-1,1-dibromocyclopropane (2.00 g, 6.03 mmol) in 15 mL of anhydrous ether was added a 1.6 M solution of methyllithium in ether (4.88 mL, 7.80 mmol) under argon at −40 °C within 15 min. Stirring was continued for 90 min, the temperature of the reaction mixture was raised to 0 °C, and water (15 mL) was added slowly. After extraction with ether, the combined organic layers were dried (magnesium sulfate) and concentrated in vacuo, yielding 2.1 g (78%) of a pale yellow solid: IR (CCl_4) ν 1955 cm^{-1}; ^1H NMR (250 MHz) δ 1.75 (d, J = 7.5 Hz, 3H), 2.05 (d, J = 3.5 Hz, 3H), 3.77 (s, 3H), 5.38 (qq, J_q = 7.5 Hz, J_q = 3.5 Hz, 1H), 6.85 (m, 2H), 7.31 (m, 2H); E_{pa} = 0.93 V (acetonitrile); HRMS calcd for $C_{12}H_{14}O$ (M^+) 174.1045, found 174.1050.

4-(4-Methoxyphenyl)-2,3-pentadienoic Acid Ethyl Ester (1d).[27] To a mixture of sodium hydride (4.80 g, 200 mmol) and 500 mL of dimethoxyethane (distilled from calcium hydride) was added triethyl phosphonoacetate (23.6 g, 108 mmol) under nitrogen at 0 °C. After 60 min, when the evolution of gas had stopped, the remaining sodium hydride was filtered off via Schlenk techniques. The yellow filtrate was heated to reflux for 5 min, and at once (4-methoxyphenyl)-methylketene[9] (17.9 g, 111 mmol) dissolved in 50 mL of dimethoxyethane (refluxed from calcium hydride) was added under nitrogen. Heating was continued for 45 min, and the mixture was poured into 1.2 L of a 2% potassium bicarbonate solution. After extraction with ether, the organic layers were dried (magnesium sulfate) and concentrated by rotary evaporation. The remaining oil was chromatographed over silica gel (Baker 0.063–0.200; cyclohexane:ethyl acetate = 1:1; R_f = 0.65) to afford 7.7 g of **1d** (30%): IR (CCl_4) ν 1943 cm^{-1}; ^1H NMR (250 MHz) δ 1.26 (t, J = 7.0 Hz, 3H), 2.15 (d, J = 3.5 Hz, 3H), 3.79 (s, 3H), 4.19 (q, J = 7.0 Hz, 2H), 5.85 (q, J = 3.5 Hz, 1H), 6.86 (m, 2H), 7.28 (m, 2H); E_{pa} = 1.11 V (acetonitrile); HRMS calcd for $C_{14}H_{16}O_3$ (M^+) 232.1099, found 232.1098.

4-(4-Methoxyphenyl)-2,3-pentadienol (1e). To a solution of **1d** (1.70 g, 7.33 mmol) in benzene (60 mL) was added a 1 M solution of diisobutylaluminum hydride in hexane (14.7 mL, 14.7 mmol) under argon within 30 min at room temperature, whereupon the color changed from yellow to light red. After 10 min the reaction was quenched first by addition of methanol and then of water, and the mixture was extracted three times with methylene chloride. The combined organic layers were dried (sodium sulfate) and concentrated in vacuo to yield 2.0 g of a yellow oil that was chromatographed twice over silica gel (Baker 0.063–0.200; (a) cyclohexane:ethyl acetate = 1:1, R_f = 0.65; (b) methylene chloride:ethyl acetate = 10:1, R_f = 0.43) to afford 280 mg of **1e** (20 %) as a yellow solid: IR (CCl_4) ν 1955 cm^{-1}; ^1H NMR (250 MHz) δ 2.13 (d, J = 3.0 Hz, 3H), 3.84 (s, 3H), 4.21 (d, J = 6.0 Hz, 1H), 4.23 (d, J = 6.0 Hz, 1H), 5.67 (ddq, J_d = 6.0 Hz , J_d = 6.0 Hz , J_q = 3.0 Hz, 1H), 6.89 (m, 2H), 7.35 (m, 2H); E_{pa} = 0.95 V (acetonitrile); HRMS calcd for $C_{12}H_{14}O_2$ (M^+) 190.0994, found 190.1001.

1,1-Bis(4-methylphenyl)allene (1f) was synthesized from 1,1-bis(4-methylphenyl)ethene according to a literature procedure.[10b]

Norbornenes 3a–e,4a–e. For the preparation of all norbornenes, a solution of **ET1** in acetonitrile was added within 15–30 min to a solution of allene **1**, diene **2a**, and base **5** (except for **3d,4d**) in the appropriate solvent at 0 °C. Stirring was continued for about 30–45 min, and the reaction was quenched and worked up as described later on for the preparation of **3c,4c**. The crude products were chromatographed over silica gel and further purified by preparative HPLC. Discrepancies between isolated yields and yields measured by means of internal standard are due to the fact that not all product containing fractions have been worked up. For most preparative reactions not the optimum ratio of allene **1**:**ET1** = 5:1 was used for economical reasons.

Norbornenes 3c,4c. A solution of **ET1** (331 mg, 633 μmol) in 5.0 mL of acetonitrile was added within 20 min to a mixture

(23) Röck, M. *Dissertation*, Freiburg, 1994, 151; to obtain potentials vs SCE simply add +0.39 V.

(24) (a) Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3567–3577. (b) Levis, M.; Lüning, U.; Müller, M.; Schmittel, M.; Wöhrle, C. *Z. Naturforsch.* **1994**, *49b*, 675–682.

(25) Seymour, D.; Volfstein, K. *J. Am. Chem. Soc.* **1948**, *70*, 1177–1179.

(26) Kostikov, R.; Molchinov, A.; Nagy, S. *J. Org. Chem. USSR* **1983**, *11*, 1291–1297.

(27) (a) Kresze, G.; Runge, W.; Ruch, E. *Liebigs Ann. Chem.* **1972**, *756*, 112–127. (b) Wadsworth, W. S.; Emmons, W. D. *J. Am. Chem. Soc.* **1961**, *83*, 1733–1738.

of **1c** (482 mg, 2.77 mmol), **2a** (108 mg, 790 μmol), and **5** (124 mg, 650 μmol) in 5.0 mL of acetonitrile, held at 0 °C under argon. The color of the solution changed during addition from deep blue to brown. After stirring for 45 min at 0 °C, the reaction was quenched by addition of a 2 N sodium methoxide solution in methanol. Thereafter a saturated sodium bicarbonate solution and methylene chloride were added, and the combined organic layers were dried (sodium sulfate). The solvent was evaporated, furnishing a brown oil that was concentrated by Kugelrohr distillation (5 h; 0.1 Torr; 70 °C). The remainder was chromatographed over silica gel (Baker 0.063–0.200; cyclohexane:methylene chloride = 5:1; R_f = 0.50) followed by preparative HPLC several times (Merck LiChrosorb Si 60/7 μm; silica gel; diameter = 25 mm; hexane:methylene chloride = 95:5; flow = 2.0 mL/min; t_R = 60–73 min) yielding 45 mg of pure **3c** (19%) and 96 mg of a mixture of **3c,4c** (39%). **Data for 3c**: mp 87 °C; ^{1}H NMR (250 MHz) δ 0.57 (q, J = 1.5 Hz, 3H, 11-H), 0.68 (d, J = 7.0 Hz, 3H, 13-H), 0.96 (s, 3H, 10-H), 1.07 (s, 3H, 8-H), 1.34 (d, J = 7.0 Hz, 3H, 15-H), 1.46 (q, J = 1.5 Hz, 3H, 12-H), 1.53 (s, 3H, 9-H), 1.87 (q, J = 7.0 Hz, 1H, 7-H), 3.77 (s, 3H, OCH_3), 5.22 (q, J = 7.0 Hz, 1H, 14-H), 6.70 (m, 4H, aryl-H, coalescence); ^{13}C NMR (100 MHz) δ 8.7, 9.4, 9.7, 11.3, 12.6, 15.1, 21.7, 53.1, 55.1, 56.9, 57.9, 60.1, 111.1, 111–113 (coalescence), 127–130 (coalescence), 131.3, 136.5, 137.8, 153.4, 157.2; MS-EI (70 eV) m/z (rel intensity) 310 (6, M^+), 136 (100). Anal. Calcd for $C_{22}H_{30}O$: C, 85.11; H, 9.73. Found: C, 85.23, H, 9.63. **Data for 4c**: ^{1}H NMR (250 MHz) δ 0.54 (d, J = 7.0 Hz, 3H, 13-H), 0.70 (s, 3H, 10-H), 1.10 (s, 3H, 8-H), 1.35 (s, 3H, 9-H), 1.35 (d, J = 7.0 Hz, 3H, 15-H), 1.48 (q, J = 1.5 Hz, 3H, 11-H), 1.63 (q, J = 1.5 Hz, 3H, 12-H), 1.78 (q, J = 7.0 Hz, 1H, 7-H), 3.80 (s, 3H, OCH_3), 5.28 (q, J = 7.0 Hz, 1H, 14-H), 6.78 (m, 2H, aryl-H), 7.23 (m, 2H, aryl-H); ^{13}C NMR (100 MHz) δ 7.9, 8.3, 9.2, 9.4, 11.4, 12.8, 24.2, 54.6, 55.5, 56.9, 57.2, 59.6, 111.7, 112.3, 129.9, 133.9, 135.7, 137.4, 154.1, 157.2. Anal. Calcd for $C_{22}H_{30}O$: C, 85.11; H, 9.73. Found: C, 85.05; H, 9.71.

Nortricyclanes 6a,b. Both nortricyclanes were prepared in the same way—as described for **6a**—either from the reaction of allenes **1a** or **1b** with diene **2a** and **ET1** in the absence of base **5** or from acid-catalyzed rearrangement of norbornenes **3a** or **3b** in $CDCl_3$.

Nortricyclane 6a. A solution of **ET1** (35.9 mg, 68.6 μmol) in 0.4 mL of acetonitrile was added within 2 min to a solution of **1a** (33.0 mg, 206 μmol) and **2a** (9.35 mg, 68.6 μmol) in 0.4 mL of acetonitrile held at 0 °C under argon. When addition was complete, the deep blue mixture was stirred for 5 min at 0 °C, quenched, and worked up as usual providing a pale green oil. Analysis of the crude product mixture by ^{1}H NMR showed that besides 37% of **3a,4a** 43% of **6a** had been formed. Furthermore, **6a** could also be prepared by stirring a solution of pure **3a** in chloroform-d_1 for several days at room temperature, affording a mixture of **6a:3a** = 2:1 that was used for characterization of **6a** since separation of the two compounds could not be achieved despite several attempts. **Data for 6a**: ^{1}H NMR (250 MHz) δ 0.65 (s, 3H, 12-H), 0.68 (d, J = 7.0 Hz, 3H, 13-H), 1.02 (s, 3H, 11-H), 1.06 (s, 3H, 10-H), 1.13 (s, 3H, 9-H), 1.22 (s, 3H, 14-H), 1.86 (q, J = 7.0 Hz, 1H, 7-H), 3.75 (s, 3H, OCH_3), 4.04 (d, $J \ll$ 1.0 Hz, 1H, 8-H_a), 4.42 (d, $J \ll$ 1.0 Hz, 1H, 8-H_b), 6.74 (m, 2H, aryl-H), 7.00 (m, 2H, aryl-H); ^{13}C NMR (100 MHz) δ 6.4, 6.6, 7.6, 8.9, 11.1, 17.7, 31.2, 34.4, 39.3, 45.3, 46.3, 52.3, 55.1, 97.4, 112.8, 130.0, 131.3, 161.3, 162.8; MS-EI (70 eV) m/z (rel intensity) 296 (31, M^+), 281 (32), 267 (13), 253 (7), 239 (12), 227 (7), 225 (12), 213 (12), 209 (6), 200 (5), 193 (6), 188 (6), 175 (16), 173 (27), 161 (57), 148 (43), 141 (7), 136 (17), 135 (100), 121 (36), 119 (26), 115 (13), 105 (28); MS-CI (isobutane) m/z (rel intensity) 298 (24, $M^+ + 2$), 297 (100, $M^+ + 1$).

Alkene 7 and Indene 8. Allene **1f** (590 mg, 2.68 mmol) and diene **2a** (91.3 mg, 670 μmol) were dissolved in 8.0 mL of methylene chloride at room temperature under argon, the solution was cooled down to 0 °C, and a solution of **ET1** (263 mg, 503 μmol) in 4.0 mL of methylene chloride was added within 25 min. Initially the color of the mixture changed from deep blue to green and then back to blue. When addition was complete, the blue mixture was stirred for 1 h at 0 °C, quenched, and worked up as usual. The remaining light brown solid was chromatographed over silica gel (Baker 0.063–0.200, cyclohexane:methylene chloride = 3:1, R_f = 0.40–0.50) followed by preparative HPLC (Merck LiChrosorb Si 60/7 μm; silica gel; diameter = 25 mm; hexane:methylene chloride = 8:2; flow = 2.0 mL/min; t_R = 17–24 min), yielding 149 mg of crude **7** and **8** (62%). Further HPLC (Merck LiChrosorb Si 60/7 μm; silica gel; diameter = 25 mm; hexane:methylene chloride = 9:1; flow = 1.0 mL/min; t_R = 36–45 min) allowed for isolation of 21 mg of pure **8** (9%) and 99 mg of a mixture of **7,8** (1.2:1, 42%). **Data for 7**: IR (CCl_4) ν 3090 cm^{-1}; ^{1}H NMR (250 MHz) δ 0.94 (s, 3H, 23-H), 1.24 (s, 6H, 24-H, 27-H), 1.70 (s, 6H, 25-H, 26-H), 2.20 (s, 6H, 2 × p-CH_3), 3.79 (s, 1H, 8-H), 4.96 (s, 1H, 2-H_a), 5.29 (s, 1H, 2-H_b), 6.85 (m, 4H, aryl-H), 6.92 (m, 4H, aryl-H); MS-EI (70 eV) m/z (rel intensity) 356 (12, M^+), 136 (100); HRMS calcd for $C_{27}H_{32}$ (M^+) 356.2504, found 356.2494. **Data for 8**: ^{1}H NMR (250 MHz) δ 0.74 ppm (s, 3H, 23-H), 0.82 (d, J = 7.0 Hz, 3H, 27-H), 0.84 (d, J = 7.0 Hz, 3H, 26-H), 1.35 (q, J < 1.0 Hz, 3H, 24-H), 1.39 (q, J < 1.0 Hz, 3H, 25-H), 1.85 (m, 1H, 22-H), 1.92 (m, 1H, coalescence, 21-H), 2.29 (s, 3H, 10-H), 2.32 (s, 3H, p-CH_3), 3.24 (d, J = 22.4 Hz, 1H, 1-H_a), 3.45 (d, J = 22.4 Hz, 1H, 1-H_b), 6.60 (d, J = 7.0 Hz, 1H, 4-H), 6.90 (d, J = 7.0 Hz, 1H, 5-H), 7.06 (m, 4H, aryl-H), 7.14 (s, 1H, 7-H); MS-EI (70 eV) m/z (rel intensity) 356 (13, M^+), 137 (100); HRMS calcd for $C_{27}H_{32}$ (M^+) 356.2504, found 356.2490.

Alkenes *E*-9 and *Z*-9 were obtained during the preparation of **3d,4d**. Separation of ***E*-9** and ***Z*-9** was achieved by preparative HPLC (Merck LiChrosorb Si 60/7μm; silica gel; diameter = 25 mm; methylene chloride; flow = 1.0 mL/min; t_R = 102 min) by taking small fractions. Thus 16 mg (13%) of pure ***E*-9** and 9 mg (7%) of a mixture of ***E*-9:*Z*-9** = 3:1 were afforded. **Data for *E*-9**: IR (CCl_4) ν 1732 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.01 (s, 3H, 13-H), 1.15 (t, J = 7.0 Hz, 3H, 7-H), 1.73 (q, J < 1.0 Hz, 3H, 15-H), 1.76 (q, J < 1.0 Hz, 3H, 16-H), 1.82 (s, 3H, 14-H), 1.83 (s, 3H, 17-H), 2.02 (d, J < 1.0 Hz, 3H, 5-H), 3.53 (d, J = 10.5 Hz, 1H, 2-H), 3.80 (s, 3H, OCH_3), 4.01 (m, 2H, 6-H), 5.68 (qd, J_d = 10.5 Hz, J_q < 1.0 Hz, 1H, 3-H), 6.85 (m, 2H, aryl-H), 7.27 (m, 2H, aryl-H); MS-EI (70 eV) m/z (rel intensity) 368 (4, M^+), 159 (100); HRMS calcd for $C_{24}H_{32}O_3$ (M^+) 368.2351, found 368.2356. **Data for *Z*-9**: ^{1}H NMR (400 MHz) δ 0.82 ppm (s, 3H, 13-H), 1.17 (t, J = 7.0 Hz, 3H, 7-H), 1.61 (s, 6H), 1.72 (d, J < 1.0 Hz, 6H), 2.00 (d, J < 1.0 Hz, 3H, 5-H), 3.20 (d, J = 10.5 Hz, 1H, 2-H), 3.83 (s, 3H, OCH_3), 4.01 (m, 2H, 6-H), 5.36 (qd, J_d = 10.5 Hz, J_q < 1.0 Hz, 1H, 3-H), 6.86 (m, 2H, aryl-H), 7.03 (m, 2H, aryl-H); MS-EI (70 eV) m/z (rel intensity) 368 (3, M^+),159 (100); HRMS calcd for $C_{24}H_{32}O_3$ (M^+) 368.2351, found 368.2352.

^{1}H NMR NOE Experiments. The difference NOE experiments have been recorded with a 400-MHz instrument using argon-saturated solutions of the substrates in chloroform-d_1. Some of the relevant NOE effects are depicted in the following manner (for numbering, see Chart 2): →irradiated H (+ = positive NOE effect; neg. = negative NOE effect). **3c**: →7-H (+ 8-H, 10-H, 13-H), →8-H (+ 7-H, 12-H, 13-H, 14-H, neg. 9-H, 15-H), →9-H (+ 7-H), →11-H (+ aryl-H), →12-H (+ aryl-H), →14-H (+ 8-H), →15-H (+ aryl-H), →aryl-H (+ 11-H, 12-H, 14-H, 15-H). **6a**: →7-H (+ 14-H), →8-H_a (+ 12-H), →8-H_b (+ 9-H), →9-H (+ 8-H_b, 10-H, 11-H, neg. 8-H_a), →10-H (+ 11-H), →11-H (+ 9-H, 10-H, 14-H). **7**: →2-H_a (+ 2-H_b, 23-H), →2-H_b (+ 2-H_a, 8-H, aryl-H).

Mechanistic Studies. (a) Thermal Cycloadditions. A solution of **1b** (65.4 mg, 454 μmol) and **2a** (61.6 mg, 454 μmol) in 1.0 mL of argon-saturated toluene was heated to reflux. After 90 min, 6 h, 18 h, 2 d, and 6 d, samples were taken and analyzed by ^{1}H NMR vs acetophenone as internal standard. It was found that with reaction time the amount of polymers increased, while **1b** was decomposed. The best yield of **3b,4b** (2%) was obtained after 18 h. In analogous reactions of **1a**, **1c**, and **1f** with **2a**, none of the corresponding norbornenes were obtained.

(b) Cycloaddition in the Presence of One-Electron Oxidants. All reactions were performed in septum-closed Schlenk tubes under argon. Via syringe techniques a solution of allene, diene, and **5** in the appropriate solvent (acetonitrile, methylene chloride) was placed in the tube. Unless noted differently, a solution or a suspension of the one-electron oxidant was added dropwise at 0 °C within 2 min. Thereafter

the reaction mixture was stirred for 5 min and finally quenched by dropwise addition of a 2 N $NaOCH_3/CH_3OH$ solution, followed by addition of saturated $NaHCO_3$ solution. The products were extracted three times using a total of about 50 mL of methylene chloride. The combined organic layers were dried over sodium sulfate, and the solvent was removed in vacuo. To the crude mixture was added a known amount of an internal standard (*m*-nitroacetophenone, acetophenone) and the mixture was analyzed by ^1H NMR and GC. When **ET3** or **ET4** was used as the one-electron oxidant, the reaction mixture was stirred for 5 min at 0 °C and for 15 min at room temperature before being quenched by addition of 0.5 mL of methanol. After removal of all volatile compounds the remainder was extracted with benzene to allow for the separation of the iron salts by filtration. Thereupon the solvent was removed and the crude mixture was analyzed as mentioned above. The results of all electron transfer initiated reactions are summarized in Tables 1–4.

(c) Reactions with 2b. Norbornene d_1-3c and d_1-4c. To a solution of **1c** (71.9 mg, 413 μmol), **2b** (11.3 mg, 82.6 μmol), and **5** (17.2 mg, 90.0 μmol) in 0.4 mL of acetonitrile, held at 0 °C under argon, was added within 2 min a solution of **ET1** (43.2 mg, 82.6 μmol) in 0.4 mL of acetonitrile, whereupon the color of the blue mixture initially changed to brown. After stirring for 5 min at 0 °C, the blue mixture was quenched and worked up as usual. The remaining green oil contained 61% of d_1-**3c** and 13% of d_1-**4c**. Both isomers were characterized from the crude mixture. MS-EI (70 eV): *m/z* (rel intensity) 311 (3, M^+), 175 (2), 174 (3), 159 (5), 138 (11), 137 (100), 136 (7), 128 (2), 123 (3), 122 (27). **Data for d_1-3c**: ^1H NMR (250 MHz) δ 0.57 (q, J = 1.5 Hz, 3H, 11-H), 0.68 (s, 3H, 13-H), 0.96 (s, 3H, 10-H), 1.07 (s, 3H, 8-H), 1.34 (d, J = 7.0 Hz, 3H, 15-H), 1.46 (q, J = 1.5 Hz, 3H, 12-H), 1.53 (s, 3H, 9-H), 3.77 (s, 3H, 22-H), 5.22 (q, J = 7.0 Hz, 1H, 14-H), 6.70 (m, 4H, aryl-H, coalescence).

Alkene d_1-7. A solution of 26.3 mg (50.4 μmol) of **ET1** in 0.4 mL of acetonitrile was added within 2 min to a solution of 55.4 mg (252 μmol) of **1f**, 6.92 mg (50.4 μmol) of **2b**, and 10.5 mg (55.0 μmol) of **5** in a mixture of 0.4 mL of acetonitrile and 0.4 mL of methylene chloride held at 0 °C under argon. During addition, the color of the solution changed from deep blue to light blue and back. After stirring for 5 min at 0 °C, the purple mixture was quenched and worked up as described above, yielding 7% of d_1-**7** (characterized from the crude mixture): ^1H NMR (250 MHz) analogous to the spectra of **7**, except for the absence of the singlet at 3.79 ppm (8-H); MS-EI (70 eV): *m/z* (rel intensity) 357 (4, M^+), 288 (7), 287 (31), 286 (5), 284 (8), 269 (10), 138 (6), 137 (42), 136 (5), 135 (5), 134 (4), 122 (9), 119 (19), 44 (100).

Indene d_1-8. To a solution of 77.4 mg (352 μmol) of **1f** and 9.66 mg (70.4 μmol) of **2b** in 0.4 mL of methylene chloride was added at 0 °C within 2 min under argon a solution of 36.8 mg (70.4 μmol) of **ET1** in 0.4 mL of acetonitrile, whereupon the color of the mixture changed from deep blue to green-blue. Stirring was continued for 5 min at 0 °C, and the reaction mixture was quenched and worked up as usual, providing a green oil. ^1H NMR showed 8% of **7** and 16% of d_1-**8**. **Data for d_1-8**. ^1H NMR (100 MHz): δ 0.74 ppm (s, 3H, 23-H), 0.82 (d, J = 7.0 Hz, 3H, 27-H), 0.84 (s, 3H, 26-H), 1.35 (q, J < 1.0 Hz, 3H, 24-H), 1.39 (q, J < 1.0 Hz, 3H, 25-H), 1.85 (m, 1H, 22-H), 2.29 (s, 3H, 10-H), 2.32 (s, 3H, *p*-CH_3), 3.24 (d, J = 22.4 Hz, 1H, 1-H_a), 3.45 (d, J = 22.4 Hz, 1H, 1-H_b), 6.60 (d, J = 7.0 Hz, 1H, 4-H), 6.90 (d, J = 7.0 Hz, 1H, 5-H), 7.06 (m, 4H, aryl-H), 7.14 (s, 1H, 7-H).

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Supporting Information Available: ^1H NMR spectra are available for **1c**, **4a**, **3b**, **4b**, **4d**, d_1-**3c**, d_1-**7**, and d_1-**8** and ^{13}C NMR spectra for **1c**, **1d**, **1e**, **3a**, **3d**, **3e**, **4e**, **6a**, **6b**, **8**, **7**, *E*-**9**, and *Z*-**9**. The following data are also available: ^1H NMR for **1a, 1b, 1f, 3a, 4a, 3b, 4b, 3d, 4d, 3e, 4e, 6b,** d_1-**4c**; ^1H NMR NOE for **3a, 3b, 3d, 6b, 8,** *E*-**9**; ^{13}C NMR for **1c, 1d, 1e, 3a, 4a, 3b, 4b, 3d, 4d, 3e, 4e, 6b, 7, 8,** *Z*-**9,** *E*-**9**; MS, HRMS for **3a, 3b, 3d, 3e, 6b** (33 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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