Tetrahedron Letters, Vol. 34, No. 52, pp. 8431-8434, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

Electron Transfer Initiated Diels-Alder Reaction with Allenes as Dienophiles[1]

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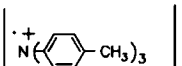
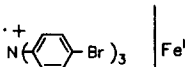
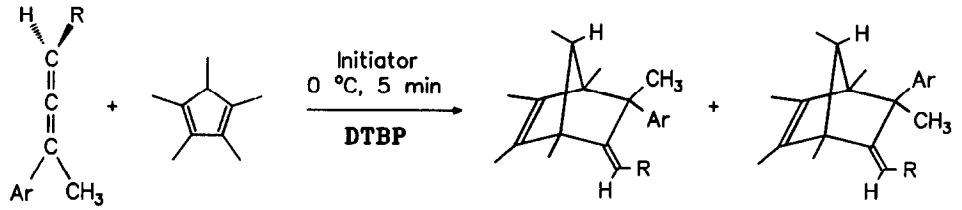
Abstract: The first examples of using aryl allenes as dienophiles in the electron transfer induced Diels-Alder reaction are described. According to mechanistic tests the reaction proceeds via a cycloaddition of the diene$^{+\bullet}$ to the allene.

The last decade has witnessed the pioneering work of Bauld[2] and others[3] on the cation radical catalyzed Diels-Alder reaction that exploits the extraordinary power of electron transfer activation in accelerating pericyclic processes. Synthetically interesting applications of this methodology, e.g. to cycloadd dienophiles that do not react in the classical thermal Diels-Alder format, were recently developed for indoles[4] and ketenes[5]. Herein, we describe our results to accomplish the Diels-Alder reaction of electron rich allenes with electron rich dienes via electron transfer initiation, an hitherto unknown reaction.[6,7]

Table 1. Redox potentials of the one-electron oxidants (vs. ferrocene/ferrocenium: $Fc/Fc^{+\bullet}$).[8]

			$Fe^{II}(phen)_3(PF_6)_3$	$Fe^{II}(4,7\text{-}phen(OMe)_2)_3(PF_6)_3$
$E_{1/2}$ [V]	0.37 **TTA$^{+\bullet}$**	0.70 **TBPA$^{+\bullet}$**	0.69 **FePhen**	0.38 **FePhenOMe**

When allenes **1a-d** were reacted thermally with pentamethylcyclopentadiene (**2**) at 120 °C for 48 h, formation of Diels-Alder products **3a-d** was observed to less than 2%, together with significant amounts of polymers. In contrast, the reaction of **1a** with **2** in the presence of aminium salts or iron(III)phenanthrolines provided good to excellent yields of *endo*- and *exo*-**3a** within 5 min at 0 °C depending on the reaction conditions (table 2). The structures of the [4+2]-cycloaddition products were assigned on the basis of IR, MS, NMR (^1H, ^{13}C) and ^1H NMR difference NOE data.[9] [2+2]-Cycloaddition products were not detected. Interestingly, the cycloaddition proceeded in a highly facioselective manner with the allene only approaching the diene from the least hindered side and with a distinct chemoselectivity for the aryl-substituted double bond.[10]



1a–1d **2** ***endo*- 3a–3d** ***exo*- 3a–3d**

a: Ar: *p*–An, R: H; **b:** Ar: *p*–An, R: CH_3; **c:** Ar: *p*–An, R: $COOC_2H_5$;
d: Ar: *p*–Tol, R: H.

Table 2. Tests to elucidate the mechanism of the cycloaddition of **1a** and **2** in the presence of various one-electron oxidants (0 °C, 5 min, acetonitrile). Analysis by ^{1}H-NMR.

ratio **1a** : **2**	initiator	mol-% of initiator	**DTBP**[a]	yield[b] [%] of *endo*-**3a**	*exo*-**3a**
1 : 1	**TTA**$^{+\cdot}$	25	+	10	2
1 : 1	**TTA**$^{+\cdot}$	100	+	54	10
3 : 1	**TTA**$^{+\cdot}$	25	+	25	5
3 : 1	**TTA**$^{+\cdot}$	100	+	58	10
3 : 1	**TTA**$^{+\cdot}$	100	-	31[c]	6[c]
3 : 1	**FePhen**	25	+	-	-
3 : 1	**FePhen**	25	-	7[d]	-
3 : 1	**FePhenOMe**	50	+	-	-
3 : 1	**FePhenOMe**	50	-	38	8
5 : 1	**TTA**$^{+\cdot}$	25	+	30	6
5 : 1	**TTA**$^{+\cdot}$[e]	25	+	46	8
5 : 1	**TTA**$^{+\cdot}$	100	+	67	13
5 : 1	**TBPA**$^{+\cdot}$	25	+	11	-

[a] **DTBP**: 2,6-di-*tert*-butylpyridine, >100 mol-% related to initiator; [b] based on diene **2**; [c] 43 % of a further isomer, that was identified as a nortricyclane derivative; [d] 14 % of a further isomer, that was identified as a nortricyclane derivative; [e] in presence of 500 mol-% **TTA** related to **TTA**$^{+\cdot}$

The mechanism of this cycloaddition reaction can be understood based on the control experiments in table 2. Since sufficiently strong one-electron oxidants (aminium salts **TTA**$^{+\cdot}$, **TBPA**$^{+\cdot}$ and the outer-sphere oxidants **FePhen**, **FePhenOMe**) successfully triggered the cycloaddition, one is led to invoke cation radicals as reactive intermediates. This assumption is further corroborated by the observation that the addition of **TTA** leads to higher yields emphasizing the importance to speed up back electron transfer to the Diels-Alder product cation radical (DA$^{+\cdot}$). According to the oxidation potentials of **1a** (table 3) vs. **2** (E_p^{ox} = 0.54 V) and the product yields as a function of the allene to diene ratio, the reaction most likely proceeds via the diene$^{+\cdot}$ in a [3+2]-cycloaddition. However, in contrast to related reactions in the literature[1] the chain length is extremely short.

[3+2] mechanism:

$$\text{diene} - e^- \rightarrow \text{diene}^{+\bullet} \quad (1)$$

$$\text{diene}^{+\bullet} + \text{allene} \rightarrow \text{DA}^{+\bullet} \quad (2)$$

$$\text{DA}^{+\bullet} + \textbf{TTA} \text{ (or diene)} \rightarrow \text{DA} + \textbf{TTA}^{+\bullet} \text{ (or diene}^{+\bullet}\text{)} \quad (3)$$

The observed cycloaddition is definitely not acid catalyzed,[11] since it proceeds both with or without added **DTBP**. However, **DTBP** prevents follow-up acid catalyzed isomerization reactions of **3** to nortricyclane derivatives.[12]

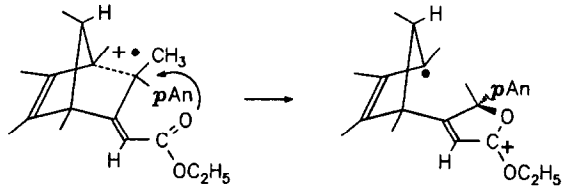
In the following, we have probed the reaction with structurally related allenes (table 3). Importantly, the cycloaddition still works out with good yields when the *p*-anisyl (*p*An) substituent is replaced by a *p*-tolyl group (*p*Tol) and when a third substituent (alkyl) is added at the allene, although the difference in oxidation potentials of the two reactants amounts to 0.7 V.

Table 3. $\textbf{TTA}^{+\bullet}$-Initiated Diels-Alder-cycloaddition of electron-rich allenes **1** with diene **2**[a] (5 min, 0 °C, isolated yields).

Allenes **1** Ar	R	E_p^{ox} [V]	Solvent	Yield of **3**[b] [%]
a: *p*An	H	0.94	CH_3CN	80[c]
b: *p*An	CH_3	0.83	CH_3CN	58
c: *p*An	$CO_2C_2H_5$	1.11	CH_3CN	<1[d], 10[e]
d: *p*Tol	H	1.23	CH_3CN/CH_2Cl_2[f]	70

[a] A ratio **1** : **2** = 5 : 1 was employed; 100 mol% of $\textbf{TTA}^{+\bullet}$ and 110 mol% of **DTBP** in relation to diene **2**. [b] For all examples an *endo* : *exo* ratio of 5 : 1 was observed. [c] Analysis by ^{1}H-NMR. [d] Identified by GC/MS. [e] Without **DTBP**. [f] 1 : 1.

The failure to obtain significant cycloaddition with allene **3c** (<1%) may be explained by the following hypotheses: (a) either the closed structure of endo $\textbf{3c}^{+\bullet}$ is destabilized by the electron-withdrawing ester substituent or (b) intramolecular nucleophilic attack of the C=O onto the cation radical diverts it from the cycloaddition route.



endo- $\textbf{3c}^{+\bullet}$

In conclusion, electron transfer initiation has successfully been used to react the electron-rich allenes **1** with the electron-rich diene **2** to afford the [4+2]-cycloaddition products, a transformation that can not be accomplished by a thermal Diels-Alder reaction.

Acknowledgements. Financial support by the Deutsche Forschungsgemeinschaft, the Wissenschaftliche Gesellschaft Freiburg and the Fonds der Chemischen Industrie is gratefully acknowledged. In particular, we are indebted to Prof. C. Rüchardt for his continued support of our research. We thank Ingo Bohn and Michael Vario for laboratory assistance.

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8. All potentials are referenced against $Fc/Fc^{+\bullet}$: to obtain potentials vs. SCE simply add +0.39 V.
9. ^{1}H-NMR (250 MHz/ $CDCl_3$): *endo* **3a**: δ = 0.55 ppm (q, J = 1.50 Hz, 3H), 0.68 (d, J = 7.00 Hz, 3H), 0.98 (s, 3H), 1.11 (s, 3H), 1.45 (q, J = 1.50 Hz, 3H), 1.48 (s, 3H), 1.91 (q, J = 7.00 Hz, 1H), 3.76 (s, 3H), 4.64 (d, J << 1.0 Hz, 1H), 4.94 (d, J << 1.0 Hz, 1H), 6.70 (m, 2H), 7.04 (m, 2H). *exo* **3a**: δ = 0.57 ppm (d, J = 7.00 Hz, 3H), 0.77 (s, 3H), 1.13 (s, 3H), 1.27 (d, J << 1.0 Hz, 3H), 1.55 (d, J << 1.0 Hz, 3H), 1.60 (q, J < 1.0 Hz, 3H), 1.81 (q, J = 7.00 Hz, 1H), 3.78 (s, 3H), 4.64 (d, J << 1.0 Hz, 1H), 4.98 (d, J << 1.0 Hz, 1H), 6.76 (m, 2H), 7.27 (m, 2H). *endo* **3b**: δ = 0.57 ppm (q, J = 1.5 Hz, 3H), 0.68 (d, J = 7.00 Hz, 3H), 0.96 (s, 3H), 1.07 (s, 3H), 1.34 (d, J = 7.00 Hz, 3H), 1.46 (q, J = 1.50 Hz, 3H), 1.53 (s, 3H), 1.87 (q, J = 7.00 Hz, 1H), 3.77 (s, 3H), 5.22 (q, J = 7.00 Hz, 1H), 6.70 (m, 4H, coalescence). *exo* **3b**: δ = 0.54 ppm (d, J = 7.00 Hz, 3H), 0.70 (s, 3H), 1.10 (s, 3H), 1.35 (s, 3H), 1.35 (d, J = 7.00 Hz, 3H), 1.48 (q, J = 1.50 Hz, 3H), 1.63 (q, J = 1.50 Hz, 3H), 1.78 (q, J = 7.00 Hz, 1H) 3.80 (s, 3H), 5.28 (q, J = 7.00 Hz, 1H), 6.78 (m, 2H), 7.23 (m, 2H). *endo* **3d**: δ = 0.55 ppm (q, J = 1.50 Hz, 3H), 0.69 (d, J = 7.00 Hz, 3H), 1.02 (s, 3H), 1.14 (s, 3H), 1.47 (q, J = 1.50 Hz, 3H), 1.50 (s, 3H), 1.94 (q, J = 7.00 Hz, 1H), 2.28 (s, 3H), 4.66 (d, J << 1.0 Hz, 1H), 4.96 (d, J << 1.0 Hz, 1H), 6.97 (m, 2H), 7.03 (m, 2H); *exo* **3d**: δ = 0.58 ppm (d, J = 7.00 Hz, 3H), 0.78 (s, 3H), 1.16 (s, 3H), 1.30 (s, 3H), 1.50 (s, 3H), 1.62 (q, J = 1.50 Hz, 3H), 1.85 (q, J = 7.00 Hz, 1H), 2.32 (s, 3H), 4.66 (d, J << 1.0 Hz, 1H), 4.99 (d, J << 1.0 Hz, 1H), 7.04 (m, 2H), 7.25 (m, 2H).
10. The observed chemoselectivity is in line with an electron transfer pathway that usually favors the more electron rich double bond.
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(Received in Germany 13 October 1993; accepted 18 October 1993)