Tetrahedron Letters,Vol.28,No.10,pp 1081-1084,1987
Printed in Great Britain

0040-4039/87 $3.00 + .00
Pergamon Journals Ltd.

ELECTROCHEMICALLY INDUCED [4+2]-CYCLOADDITIONS - A MECHANISTIC INTERPRETATION OF THE CATION RADICAL DIELS-ALDER REACTION BASED ON PREPARATIVE RESULTS[1]

Jiri Mlcoch and Eberhard Steckhan*

Institut für Organische Chemie und Biochemie der Universität Bonn,
Gerhard-Domagk-Str. 1, D-5300 Bonn 1, BRD

Summary: For the first time it was possible to induce the cation-radical Diels-Alder reaction between electronrich dienes and electronrich dienophiles electrochemically, thus providing a clearer view upon the mechanism of this reaction type. In contrast to common explanations it could be demonstrated that this reaction most probably takes place via the cation radical of the diene. A role selectivity towards the cation radical of the dienophile could be ruled out.

Recently we reported upon the photochemically initiated electron-transfer catalyzed Diels-Alder reaction of electronrich dienophiles and dienes[2]. Triphenylpyrylium- and substituted triphenylpyrylium tetrafluoroborates are acting as sensitizers. A clear mechanistic interpretation of this reaction, however, is difficult because exciplex or triplex[3] formation together with a strong solvent effect complicates the system. This complication is eliminated, if the starting cation radical is generated electrochemically. Thus, a free cation radical can be generated selectively in presence of other oxidizable compounds. Electrochemically induced electron transfer chain reactions are known in the case of $S_{RN}1$-type reactions[4]. Cycloadditions via olefin cation radicals, however, were only observed once in the case of a [2+2]-reaction[5]. We found reaction conditions which allowed us to perform electrochemically initiated [4+2]-cycloadditions between two electron-rich components for the first time (Table 1, Table 2).

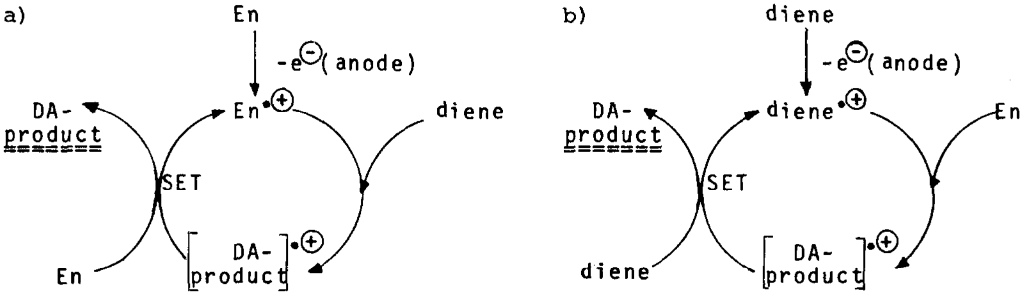
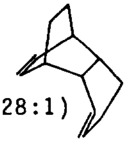
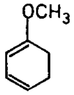
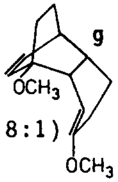
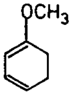
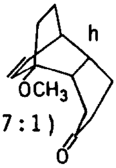
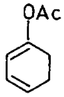
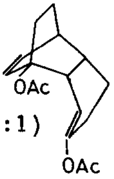


Fig.1: Alternative reaction sequences for the electrochemically initiated cation radical Diels-Alder reaction (a: via dienophile cation radical; b: via diene cation radical; En = dienophile; SET = solution electron transfer

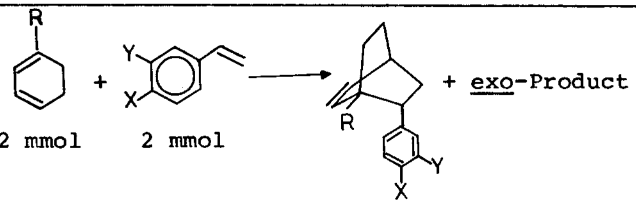
Table 1. Examples for electrochemically induced cation radical Diels-Alder dimerizations

Substrate (mmol)	E_{pox} (V)	Working Potential (V)	Charge (As)	Product [%(endo:exo)]	Comparison with Pyrylium Salt Sensitized Photo-Diels-Alder Reaction [% (endo:exo)]	Sens.
 (5)	1.08	0.8-0.85	213	 24^d(28:1)	82 (6:1) 95 (8:1)	$TPP^+BF_4^-$ [a] $TRT^+BF_4^-$ [b]
 (5)	0.53	0.3	152	 24^e(3.8:1)	39 (1:6) together with 30 % of the ketone (endo:exo = 7:1)	$TAP^+BF_4^-$ [c]
 (3)	0.53	0.35-0.4	42	 35 (3.7:1)	70 (1.2:1) 58 (2.2:1)	$TPP^+BF_4^-$ $TAP^+BF_4^-$
 (2)	0.96	0.7-0.75	235	 14^f(17:1)	54 (5:1)	$TPP^+BF_4^-$

[a] Triphenylpyrylium BF_4^-; [b] trityl BF_4^-; [c] tris(4-methoxyphenyl)pyrylium BF_4^-; [d] accompanied by 10 % benzene; [e] accompanied by 40 % methoxybenzene; [f] accompanied by 55 % phenylacetate; [g] isolated by LC on SiO_2 with diethyl ether/pentane(1:1); [h] isolated by LC on SiO_2 with CH_2Cl_2(hydrolysis of enolether)

The largest problem for the preparative application of this reaction is the tendency of olefin cation radicals to polymerize under the prevailing non-nucleophilic conditions, thus passivating the electrode surface. Therefore the reaction was performed at a very low current density so that the working potential usually is several hundred millivolts more negative than the anodic peak potential (E_{pox}). An undivided cell equipped with graphite electrodes and filled with an electrolyte consisting of CH_3CN/CH_2Cl_2(1:1; 0.1 M $LiClO_4$) was used. 2,6-Lutidine was added as it helped to prevent polymerization to a certain extent. The relatively high charge consumption indicates a short chain length presumably because of polymerization as side reaction. Nevertheless, this reaction is also of preparative interest as in the case of cross coupling Diels-Alder reactions high selectivities with respect to the cross coupling product could be obtained. In addition, the endo:exo-ratio is

Table 2. Electrochemically induced cross-Diels-Alder reactions of 1,3-cyclohexadienes and substituted styrenes



No.	Diene R=	E_{pox} [a] (V)	Styrene X=	Y=	E_{pox} [a] (V)	Working Potential (V) [a]	Charge (As)	Cross-DA-Product % (endo:exo)	Photo-DA Reaction % (endo:exo)
1	H	1.08	NO_2	H	1.8	0.85	128	---	---
2	H	1.08	Cl	H	1.49	0.9-1.0	295	11 (53:1)	7 (35:1)[b]
3	H	1.08	H	H	1.45	0.9	414	13 (19:1)	38 (10:1)[b]
4	H	1.08	CH_3	H	1.35	0.85	106	22 (9:1)	28 (4:1)[b]
5	H	1.08	OMe	H	0.98	0.7-0.8	187	14 (4:1)	24 (2.3:1)[b]
6	H	1.08	OMe	OMe	0.85	0.7-0.8	502	11 (1.9:1)	6 (1.8:1)[c]
7	H	1.08	OMe	OMe	0.85	0.6	151	10 (1.9:1)[d]	
8	H	1.08	$N(Me)_2$	H	0.26	0.15-0.4		---	---
9	OMe	0.53	OMe	OMe	0.85	0.4	264	6 (5:1)	

[a] Potential vs. Ag/$AgNO_3$-ref.-electrode; [b] triphenylpyrylium BF_4^- as sensitizer; [c] tris(4-methoxyphenyl)pyrylium BF_4^- as sensitizer; [d] 62 % cyclohexadiene recovered; only traces of dicyclohexadiene present.

Table 3. Optimization of cross-Diels-Alder products in the electrochemically initiated cation radical Diels-Alder reaction

Substrates 1,3-Cyclohexadiene (mmol)	Styrene (mmol)	Working Potential[a] (V)	Temperature (°C)	Cross-DA Product % (endo:exo)	Photo-DA Reaction %(endo:exo)
2.5	2.5	0.9	20	13 (19:1)	
2.5	5.0	0.8-0.9	20	21 (18:1)	38 (10:1)
2.5	2.5	0.9-1.0	-40	22 (25:1)	
2.5	10.0	1.0	-40	33 (30:1)	

[a] otential vs. Ag/$AgNO_3$-ref.-electrode.

enhanced drastically as compared with the photochemical initialization. Optimization of the yields is still possible as shown in the case of the reaction between 1,3-cyclohexadiene and styrene (Table 3) by lowering the reaction temperature and increasing the concentration of the styrene.

In the cross-coupling reaction between 1,3-cyclohexadiene and differently substituted styrenes under standard conditions(Table 2, No. 2-7) it is shown that interestingly the endo:exo-ratio of the product almost linearly decreases with dropping oxidation potential of the styrene. This points to the fact that the

HOMO of the styrene is important for the secondary orbital interaction. Diels-Alder reactions are not observed, if the oxidation potentials of the diene and the dienophile are too much apart (Table 2, No. 1 and 8). Bauld et al.[6] using tris(4-bromophenyl)ammoniumyl $SbCl_6^-$ as oxidant for the initiation of this reaction arguments, that the cycloaddition via the cation radical of the dienophile (Fig. 1a) is an allowed pericyclic reaction, while that via the cation radical of the diene (Fig. 1b) is forbidden. This explanation seems not to be correct in the case of the electrochemically initiated Diels-Alder reaction. The first indication for a reaction via the cation radical of the diene was, that in the case of the reaction between p-chlorostyrene and 1,3-cyclohexadiene (Table 2, No. 2) the product can be obtained at a potential, which is about 0.5 V more positive than the oxidation potential of the styrene The strongest proof, however, is given by the result of a three component cross-reaction. It was shown that 1,3-cyclohexadiene as well as 1-methoxy-1,3-cyclohexadiene are both forming Diels-Alder products with 3,4-dimethoxystyrene as dienophile (Table 2, No. 7 and 9). If the reaction is performed with all three components present at a working potential (0.35-0.4 V), which is considerably lower than the anodic peak potential of the three compounds, only the cross-Diels-Alder product between 1-methoxy-1,3-cyclohexadiene and 3,4-dimethoxystyrene is formed in 6% yield (endo:exo = 5:1). This is strong evidence for the fact that the cation radical of 1-methoxy-1,3-cyclohexadiene is the key intermediate in the electron transfer chain reaction according to Fig. 1b. If the reaction would proceed via the cation radical of the styrene, which has an oxidation potential between those of the two dienes, the Diels-Alder product with 1,3-cyclohexadiene should have been observed also. Therefore a role selectivity in preference of the cation radical of the dienophile as proposed by Bauld[6] can be ruled out. This statement is supported by the result of a second three component competition experiment: 3,4-dimethoxystyrene together with p-chlorostyrene, which both give cross-coupling products with 1,3-cyclohexadiene in a two component reaction (Table 2, No.2 and 7), are electrolyzed at 0.7 V in presence of 1,3-cyclohexadiene. In this case both cross-coupling products are formed. Therefore the cation radical of 1,3-cyclohexadiene with its oxidation potential between those of the two styrenes must be the key intermediate.

Acknowledgment: Financial support by the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen and the Fonds der Chemischen Industrie is gratefully acknowledged.

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1 In part presented at the 1st Int. Symp. on Electroorganic Synthesis, Kurashiki, Japan, Oct. 31 - Nov. 3, 1986.

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(Received in Germany 5 December 1986)