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Cycloaddition of *o*-Quinodimethanes Generated from 1,2-Bis(bromomethyl)benzenes by Constant-Current Electroreduction

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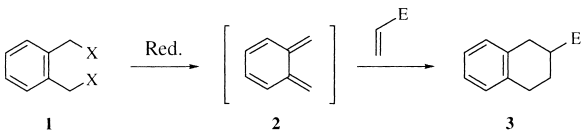
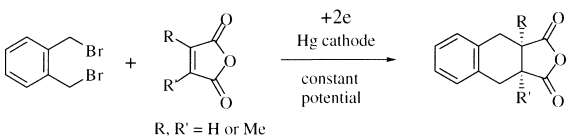
The constant-current electroreduction of 1,2-bis(bromomethyl)benzenes with dienophiles in NH_4NO_3–MeOH gave Diels–Alder cycloadducts in moderate-to-good yields.

o-Quinodimethanes are useful intermediates in organic synthesis.[1] The reductive dehalogenation of 1,2-bis(halomethyl)benzenes **1** seems to be the most convenient and simplest method to generate *o*-quinodimethanes **2** (Scheme 1). For this purpose, several reducing agents such as Zn,[2] Fe,[3] Cu,[4] Cr^{II},[5] Ni[6] and NaI[7] have been reported. On the other hand, electroreduction is expected to be a versatile method for the reduction of 1,2-bis(halomethyl)benzenes without using such reducing agents under milder conditions. Covitz has reported that the electroreduction of 1,2-bis(bromomethyl)benzene in DMF using a Hg cathode gave poly(*o*-phenyleneethylene) in 50% yield.[8] Recently, Utley and his co-workers have reported that the electroreduction of 1,2-bis(bromomethyl)benzenes and maleic anhydrides in Et_4NBr–DMF using a Hg cathode produced the corresponding Diels–Alder cycloadducts in moderate-to-good yields (Scheme 2).[9] However, dienophiles other than maleic anhydrides, such as methyl acrylate and methyl vinyl ketone, brought about poor yields of the cycloadducts;[9a] a constant-potential electrolysis was employed in this electroreduction. We therefore investigated more efficient conditions for the electroreduction of 1,2-bis(bromomethyl)benzenes with dienophiles other than maleic anhydrides using constant-current electrolysis, which is more convenient than the constant-potential method. In this paper, we report that the Diels–Alder cycloaddition of electrogenerated *o*-quinodimethanes with dienophiles, like methyl acrylate and methyl vinyl ketone, was effected by the constant-current electroreduction of 1,2-bis(bromomethyl)benzenes in NH_4NO_3–MeOH.



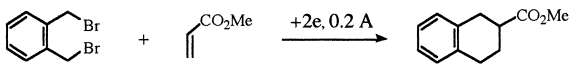
Scheme 1.



Scheme 2.

Initially, we surveyed the conditions for the constant-current electroreduction of 1,2-bis(bromomethyl)benzene (**1a**) in the presence of methyl acrylate (5 molar amounts) as a dienophile at a current of 0.2 A. The results are summarized in Table 1. The electoreduction in DMF or MeOH containing Et_4NOTs produced considerable amounts of dimethyl adipate and polymeric compounds, though the yields of cycloadduct **3a** were low (runs 1, 2). In contrast, when the reduction was carried out in NH_4NO_3–MeOH with a Pb cathode, the adduct **3a** was obtained in 67% yield, and no dimethyl adipate was formed (run 3). This result showed that only **1a** was reduced and methyl acrylate was not reduced at all under the conditions. Using DMF or EtOH as a solvent, the yield of **3a** decreased (runs 4, 5). As a supporting electrolyte, NH_4NO_3 gave a better result than the other ammonium salts (runs 6–8). Among the other cathode materials, only a carbon-felt cathode afforded a yield of **3a** comparable with that obtained from a Pb cathode (runs 9–12). When the reduction was carried out using a Pt, Zn, or Cu cathode, the formation of dimethyl adipate was observed, and the yield of **3a** somewhat decreased. This result suggests that the Pb cathode was suitable for the selective reduction of **1a**, although the reduction peak potential of **1a** could not be measured by cyclic voltammetry using a Pb cathode, unfortunately. Next, we optimized the amounts of methyl acrylate and current for electroreduction in NH_4NO_3–MeOH using a Pb cathode. As shown in Table 2, 5 molar amounts of methyl

Table 1. Constant-Current Electroreduction of 1,2-Bis(bromomethyl)benzene (**1a**) and Methyl Acrylate[a)]



1a **3a**

Run	Solvent[b)]	Cathode	Electricity (*F*/mol)	Yield[c)] of **3a**/%
1	Et_4NOTs/DMF	Pb	3.0	30
2	Et_4NOTs/MeOH	Pb	6.5	29
3	NH_4NO_3/MeOH	Pb	3.0	67
4	NH_4NO_3/EtOH	Pb	3.0	50
5	NH_4NO_3/DMF	Pb	2.5	33
6	NH_4Cl/MeOH	Pb	3.5	49
7	NH_4Br/MeOH	Pb	3.0	64
8	NH_4OAc/MeOH	Pb	3.5	50
9	NH_4NO_3/MeOH	Pt	4.0	42
10	NH_4NO_3/MeOH	Zn	5.5	23
11	NH_4NO_3/MeOH	Cu	4.0	46
12	NH_4NO_3/MeOH	Carbon-Felt	3.0	65

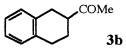
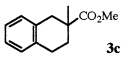
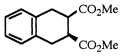
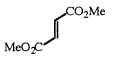
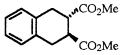
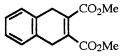
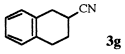
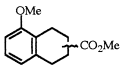
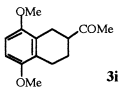
a) Electroreduction of **1a** was carried out in the presence of 5 mol. amt. of methyl acrylate at 0.2 A. b) 0.2 M Electrolyte in solvent. c) Isolated yields.

Table 2. Constant-Current Electroreduction of **1a** and Methyl Acrylate in 0.2 M NH_4NO_3/MeOH Using a Pb Cathode

Run	Methyl Acrylate/mol. amt.	Current/A	Yield[a] of **3a**/%
1	1.25	0.2	27
2	2.5	0.2	44
3	5.0	0.2	67
4	10.0	0.2	60
5	20.0	0.2	59
6	5.0	0.1	63
7	5.0	0.4	45
8	5.0	0.6	32

a) Isolated yields.

Table 3. Constant-Current Electroreduction of **1** with Dienophiles in 0.2 M NH_4NO_3/MeOH Using a Pb Cathode[a]

Run	**1**	Dienophile	Adduct (**3**)	Yield[b,c] of **3**/%	
1	**1a**		 **3b**	83	(58)
2	**1a**		 **3c**	42	
3	**1a**		 **3d**	41[d]	(23)[d]
4	**1a**		 **3e**	63	(35)
5	**1a**		 **3f**	48	
6	**1a**		 **3g**	40	(40)
7	 **1b**		 **3h**	42[e]	
8	 **1c**		 **3i**	61	

a) Electroreduction was carried out under the same conditions as run 3 in Table 1. b) Isolated yields. c) In parentheses are yields obtained with a carbon-felt cathode. d) *cis*:*trans* = 3:1 by ^{1}H NMR analysis. e) Obtained as a 2:1 mixture of two regioisomers according to ^{13}C NMR analysis.

acrylate and 0.2 A of current (4 mA/cm^2) gave the best yield of **3a**.

Table 3 presents the results of the electroreduction of 1,2-bis(bromomethyl)benzenes **1** with other dienophiles under the same conditions as in run 3 (Table 1). These results show that the constant-current electroreduction of **1** in NH_4NO_3–MeOH is also effective for the cycloaddition of electrogenerated *o*-quinodimethanes with dienophiles other than maleic anhydrides. This electrochemical method provides alternative means for the reductive generation of *o*-quinodimethanes from 1,2-bis(bromomethyl)benzenes and their subsequent cycloaddition with a variety of dienophiles without using metal reducing agents.

Experimental

Typical Procedure for Electroreduction. A solution of 0.2 M NH_4NO_3 in MeOH (40 mL) was put into a divided cell of a 50 mL beaker (4.5 cm diameter, 6 cm height) equipped with a Pb cathode (5 × 10 cm^2), a Pt anode (2 × 2 cm^2), and a cylindrical ceramic diaphragm (2.5 cm diameter, 7 cm height). To the catholyte (outside the diaphragm) was added **1a** (1.31 g, 5 mmol) and methyl acrylate (2.25 mL, 25 mmol). Electroreduction was carried out at a constant current of 0.2 A at 25 °C until 1448 C of electricity (3 *F*/mol) had passed. The catholyte was poured into water and extracted with Et_2O. The product **3a** (0.64 g, 67% yield) was isolated by column chromatography on silica gel (hexane–AcOEt).

Determination of Products. Cycloadducts **3a–i** were confirmed by a comparison of their spectroscopic data with those of authentic samples prepared by reported methods.[2,5]

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