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

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(Received July 19, 2002)

The constant-current electroreduction of 1,2-bis(bromomethyl)benzenes with dienophiles in NH₄NO₃–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 Ni⁶ and NaI⁷ 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 Et₄NBr-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 constantcurrent 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 1,2bis(bromomethyl)benzenes in NH₄NO₃–MeOH.

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 Et₄NOTs 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 NH₄NO₃-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 NH₄NO₃-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)}

∧ _{CO2}Me

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1a			3a				
Dun	Solvent ^{b)}	Cathoda	Electricity	Yield ^{c)} of			
Kun	Solvent	Cathode	(F/mol)	3a/%			
1	Et ₄ NOTs/DMF	Pb	3.0	30			
2	Et ₄ NOTs/MeOH	Pb	6.5	29			
3	NH ₄ NO ₃ /MeOH	Pb	3.0	67			
4	NH ₄ NO ₃ /EtOH	Pb	3.0	50			
5	NH ₄ NO ₃ /DMF	Pb	2.5	33			
6	NH ₄ Cl/MeOH	Pb	3.5	49			
7	NH ₄ Br/MeOH	Pb	3.0	64			
8	NH ₄ OAc/MeOH	Pb	3.5	50			
9	NH ₄ NO ₃ /MeOH	Pt	4.0	42			
10	NH ₄ NO ₃ /MeOH	Zn	5.5	23			
11	NH4NO3/MeOH	Cu	4.0	46			
12	NH ₄ NO 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 NH₄NO₃/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 NH₄NO₃/MeOH Using a Pb Cathode^{a)}

Run	1	Dienophile	Adduct (3)	Yield ^{b,c)} of 3/%
1	1a	×L	COMe 3b	83 (58)
2	1 a		CO ₂ Me	42
3	1a		CO ₂ Me CO ₂ Me 3d	41^{d_1} (23) ^{d)}
4	1a	MeO ₂ CO ₂ Me	CO2Me 3e	63 (35)
5	1 a	MeO ₂ C	CO ₂ Me CO ₂ Me 3f	48
6	1 a	CN	3g	40 (40)
7	OMe Br Br 1b	€ CO2Me	CO ₂ Me CO ₂ Me	42 ^{e)}
8	OMe Br OMe lc	Ň	OMe COMe	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 ¹H NMR analysis. e) Obtained as a 2:1 mixture of two regioisomers according to ¹³C 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 1,2bis(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 NH₄NO₃–MeOH is also effective for the cycloaddition of electrogenerated oquinodimethanes 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 NH₄NO₃ 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 cm²), a Pt anode (2 × 2 cm²), 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 Et₂O. 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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