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The Addition Reaction of Benzynes Generated Electrochemically from Dihalobenzenes with Tertiary Amines

Naoyoshi Egashira,* Jun Takenaga, and Fumiaki Hori
Department of Environmental Chemistry and Engineering, Faculty of Engineering, Oita University,
700 Dannoharu, Oita 870-11

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Synopsis. The electroreduction of dihalobenzenes was carried out in the presence of tertiary amines as benzyne acceptors in DMF-TBAP, giving the addition products in yields of more than 10%. For *o*-dibromobenzene, the yield of the addition product, *N*-phenylpiperidine, increased to 21% in the presence of *N*-ethylpiperidine.

Benzynes which undergo many types of addition reactions are uaually generated on the photolysis or pyrolysis of reactive reagents.[1] An electrolytic method can be expected to generate benzynes under mild conditions from reagents which are readily available. Wawzonek et al.[2] have reported on the generation of a benzyne in the electrolysis of *o*-dibromobenzene (**1**) in the presence of furan as a benzyne acceptor and have obtained the addition product derived from the benzyne in a 1% yield. This has been the sole report on the electrolytic generation of benzyne. We have previously reported that the yield of the addition product of the benzyne from **1** increased to 10% when *N*-ethylpiperidine (**2**) was used instead of furan.[3] In the present work, five dihalobenzenes are electrolyzed in a sufficiently dried electrolyte containing five tertiary amines; they are examined in detail for the addition products.

Compound **1** showed an irreversible cathodic peak at -3.00 V vs. Ag/Ag$^+$ in the presence of **2**. The electrolysis of **1** in the presence of a large excess of **2** was thus carried out at -3.20 V. The resulting products were bromobenzene, benzene, and an unknown compound. The unknown compound was isolated from the catholyte after electrolysis and confirmed to be *N*-phenylpiperidine (**3**) since it gave an IR spectrum identical with that of the authentic sample. The time-course of the products is shown in Fig. 1, which represents the simultaneous formation of each product. Three gaseous products containing ethylene were also detected by gas chromatography, and their amounts increased gradually. The electrolysis of bromobenzene at -3.20 V in the presence of **2** gave simply benzene; the consumption rate of bromobenzene was low, since the cathodic peak potential of bromobenzene (-3.30 V) was higher than the electrolysis potential of **1**. Furthermore, **3** was not detected in the electrolysis of **1** at -3.20 V when **2** was not added to the electrolyte. These results indicate that bromobenzene does not participate in the formation of **3** and that benzene is formed in part from **1** directly and in part through bromobenzene. It has been reported that **3** was produced through the reaction of benzyne generated in a homogeneous reaction with **2**.[1] Compound **3** is thus presumed to be produced through benzyne as depicted in Scheme 1.

The yield of **3** (14 %) is larger than that of the product through benzyne reported by Wawzonek et al.[2] Table 1 shows the effects of the electrolyte temperature, the electrolysis potential, the benzyne acceptors, and the electrode materials on the electrolysis of **1**. An appropriate potential for the electrolysis is determined to be -3.20 V because of the higher yields obtained in three experiments (Runs 1—3). A decrease in the electrolyte temperature to 20 °C lowered the yield of **3** (Run 4). When SCE was used instead

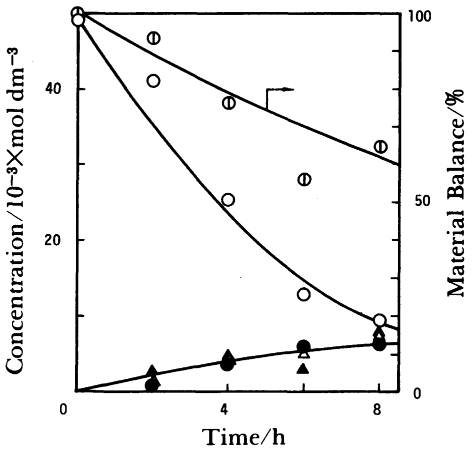
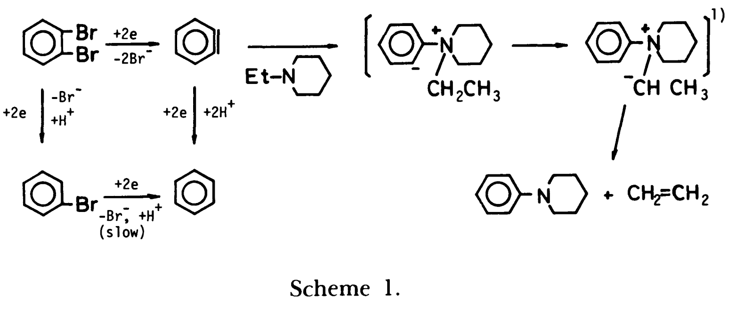
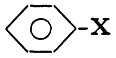
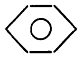


Fig. 1. Time-course of products in electrolysis of **1** in the presence of **2**. ○: material balance, ○: **1**, ●: **3**, ▲: bromobenzene, △: benzene.



Scheme 1.

Table 1. Electrolytic Results of Dihalobenzenes[a]

Run	Substrate	Benzyne acceptor	Working electrode	−E/V vs. Ag/Ag$^+$	Yield/% Addition product			Electricity F mol^{-1}
1	**1**	**2**	Pt	3.20	14(**3**)[f]	15	16	3.7
2	**1**	**2**	Pt	3.00	10(**3**)	10	21	4.2
3	**1**	**2**	Pt	3.40	11(**3**)	6.9	15	4.0
4	**1**	**2**	Pt	3.20[b]	12(**3**)	7.0	27	2.6
5	**1**	**2**	Pt	2.80[c]	6.0(**3**)	9.0	70	9.0
6	**1**	**2**[d]	Pt	3.20	21(**3**)	16	22	2.8
7	**1**	**2**	Hg	3.20	2.6(**3**)	4.0	10	2.7
8	**1**	**2**	GC	3.80	0.8(**3**)	2.0	5.0	1.6
9	**1**	*N*-Ethylmorpholine	Pt	3.20	12 (*N*-Phenylmorpholine)[e]	15	18	4.0
10	**1**	*N*-Methylpiperidine	Pt	3.20	11(**3**)	5.5	45	2.0
11	**1**	*N*-(2-Hydroxyethyl)piperidine	Pt	3.20	14(**3**)	25	36	3.1
12	**1**	Triethylamine	Pt	3.20	13 (*N*,*N*-Diethylaniline)[e]	9.5	25	3.4
13	*o*-Dichlorobenzene	**2**	Pt	3.60	2.0(**3**)	27	11	2.6
14	*o*-Diiodobenzene	**2**	Pt	3.20	14(**3**)	16	14	4.1
15	*m*-Dibromobenzene	**2**	Pt	3.20	tr(**3**)	54	22	2.5
16	*p*-Dibromobenzene	**2**	Pt	3.20	0.3(**3**)	23	19	4.6
17	**1**	—	Pt	3.20	—	2.0	24	3.0

a) Electrolysis was carried out in DMF solutions containing 5.0 cm^3 of the benzyne acceptor at 40 °C unless otherwise noted. b) The temperature was 20 °C. c) SCE was used as the reference electrode. d) 20 cm^3 of **2** was used. e) The retention time of each product, as determined by HPLC, agreed with that of an authentic sample. f) Ethylene was detected by means of gas chromatography.

of the Ag/Ag$^+$ reference electrode, the yield of **3** remarkably decreased (Run 5). This was due to a large increase in the water concentration of the electrolyte from the beginning of the electrolysis (0.010 M: 1 M = mol dm^{-3}) to the end (0.080 M); the use of an Ag/Ag$^+$ reference electrode hardly increased the water concentration at all. The further addition of **2** (20 cm^3) resulted in an increase in the yield of **3** to 21% (Run 6). Benzyne can exit in the vicinity of the electrode, as it has a short lifetime. The amount of benzyne available for the formation of the addition products may thus be smaller than that in a conventional homogeneous reaction. The disadvantage can be reduced by the use of a high concentration of a benzyne acceptor. The use of Hg and glassy carbon (GC) as working electrodes considerably decreases the yields of the products containing **3** (Runs 7 and 8). These products are perhaps attributable to the formation of mercury compounds and polymers respectively. The reaction of benzyne with several tertiary amines similarly gave the corresponding addition products, the yields of which were in the range of 11—14% (Runs 9—12). This fact suggests that the steric hindrance around nitrogen atoms of the tertiary amines against benzyne is of the same degree. Electrolysis in the presence of *N*-methylpiperidine and *N*-(hydroxyethyl)-piperidine produced methane and an unknown gaseous product respectively; the evolution mechanisms remain ambiguous. *o*-Dichlorobenzene and *o*-diiodobenzene gave the same addition product as **3** in moderate yields, while *o*-dichlorobenzene gave it in a very low yield (Runs 13 and 14). *o*-Dibromobenzene and *o*-diiodobenzene are thus thought to be suitable for the electrolytic generation of benzyne. The fact that *m*- and *p*-dibromobenzenes also give **3** is interesting, since it suggests the generation of *m*- and *p*-benzynes (Runs 15 and 16). Unfortunately, the yields of **3** for both the compounds were very low. Each electrolysis requires about 3 F mol^{-1} of electricity, except for Run 5, indicating that dihalobenzenes undergoes electroreduction with a good efficiency. The ratio of the total moles of the products containing the starting material to the original moles of the starting material, the material balance, gradually decreased (Fig. 1). This suggests that the generated intermediates, such as benzyne, radical anions, and free radicals, follow complex reactions.

Experimental

DMF was purified by a conventional method.[4] Cyclic voltammetry was carried out in the same way as in a previous work.[5] A DMF solution containing **1** (0.050 M), **2** (5.0 cm^3), and tetrabutylammonium perchlorate (TBAP, 0.10 M) was prepared. A large-scale electrolysis of the DMF solution was performed on a platinum electrode (25.5 cm^2) at 40 °C in a two-compartment cell after 6.4 g molecular sieve 4A (heated at 350 °C for 3 h) had been added to the catholyte in order to dry it. The counter and reference electrodes used were a platinum plate (1.0 cm^2) and an Ag/Ag$^+$ electrode. The outlet of nitrogen of the electrolytic cell was cooled with water in order to collect any benzene produced in the cell. After the electrolysis has finished, the catholyte was concentrated under reduced pressure, and then the residue was extracted with diethyl ether. The product was separated with TLC (SiO_2, chloroform : benzene = 8 : 2) after the ethereal solution had been evaporated. Compound **3** as an authentic sample was synthesized in the way reported by Bunnett et al.:[6] ^{1}H NMR ($CDCl_3$) δ=1.7—1.9 (6H, *m*, $-CH_2-$), 3.2—3.4 (4H, *m*, *N*-CH_2-), 6.9—7.5 (5H, *m*, Arom). The catholyte was analyzed by using HPLC (ODS, CH_3CN : H_2O = 55 : 45) in order to determine the concentrations of the products.

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