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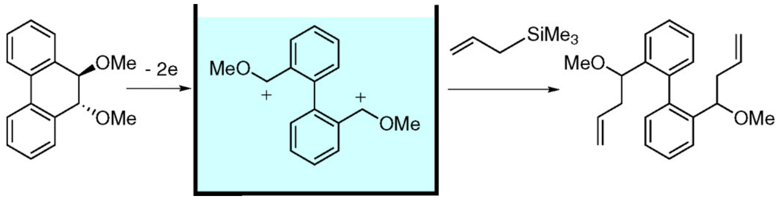

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COMMUNICATIONS

"Cation Pool" Method Based on C−C Bond Dissociation. Effective Generation of Monocations and Dications

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We have recently developed the "cation pool" method,[1] which involves the irreversible oxidative generation and accumulation of highly reactive cations in the absence of nucleophiles. Heteroatom-stabilized carbocations, such as *N*-acyliminium ion pools and alkoxycarbenium ion pools, have been generated by this method. In the first step of the cation pool method, a radical cation is generated by one-electron transfer. In the next step, a proton or a formal silyl cation is eliminated to give the carbon radical, which undergoes further one-electron oxidation to give the corresponding carbocation (Scheme 1).

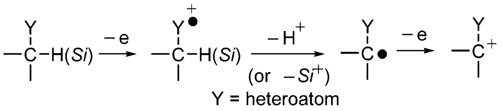
We have been interested in developing a new method for the generation of cation pools, which involves the oxidative C−C bond dissociation, because such a process is commonly observed in the decomposition of radical cations[2−4] (Scheme 2). A major advantage of this approach is easy generation of dications,[5] if we employ cyclic compounds as starting materials (Scheme 3).[6] Such dications seem to provide powerful intermediates for the construction of various organic architectures. We report here the realization of this concept.

The electrochemical oxidation of *meso*-1,2-dimethoxy-1,2-diphenylethane (**1**) was carried out in an undivided cell equipped with a carbon felt anode and a platinum plate cathode using Bu_4NBF_4/CD_2Cl_2 at −48 °C (Scheme 4). After 2.5 F/mol of electricity was consumed, the solution thus obtained (a pool of alkoxycarbenium ion **2**) was analyzed by NMR spectroscopy at 0 °C. ^1H NMR exhibited a signal at 9.87 ppm due to the methine proton. ^{13}C NMR exhibited a signal at 207.8 ppm due to the methine carbon. These chemical shifts are consistent with those of alkoxycarbenium ions generated from acetals by the treatment with a Lewis acid.[7] These values also suggest the presence of a strong positive charge at the carbon, indicating the formation of an ionic species.

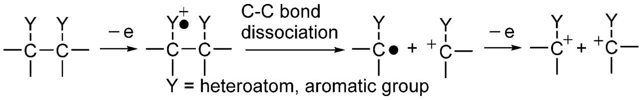
Thus, a pool of **2** was generated at −48 °C in a preparative scale in CH_2Cl_2 and was allowed to react with allyltrimethylsilane (2.5 equiv) (Scheme 4). The corresponding allylated product **3** was obtained in 90% yield based upon **1** (100% yield means that 2 mols of **2** is produced from 1 mol of **1**) (Table 1, run 2), indicating that cation **2** was effectively formed by the dissociation of the C−C bond. Although the reaction at −25 °C gave a similar result (run 3), the reaction at −78 °C resulted in lower yield of **3**, presumably because the dissociation of the C−C bond is slow at this temperature (run 1).

D,L-1,2-Dimethoxy-1,2-diphenylethane (**4**) was also effective as a precursor, although the yield of **3** was slightly lower (run 4). It is interesting to note that the electrochemical oxidation of methoxyphenylmethane (**5**) also gave **3** despite its higher oxidation potential, but the yield was somewhat lower (runs 5 and 6). The use of a silyl group as an electroauxiliary[8] decreased the oxidation potential and led to effective formation of **3** (run 7). These observations indicate that the C−C bond dissociation is comparable to, or somewhat more effective than, the C−H and C−Si bond dissociations. Compounds **7**−**9** were also examined (runs 8−13). They gave **3**, but the yields were lower.

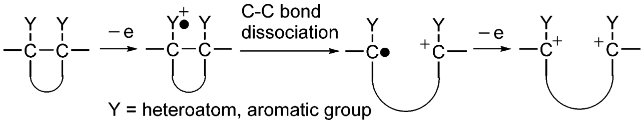
Scheme 1



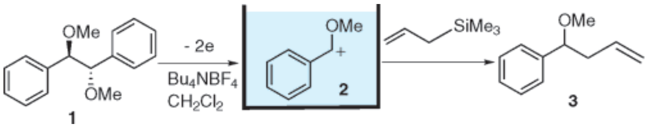
Scheme 2



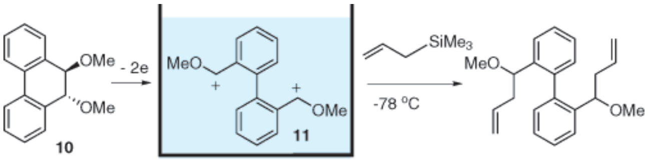
Scheme 3



Scheme 4


1
2
3

Scheme 5


10
11
12

In the next step, we examined the use of cyclic compounds as starting materials to generate dications. The anodic oxidation of compound **10** ($E_{ox} = 1.55$ V) resulted in the formation of dication **11**, which exhibited ^{13}C NMR signals at 74.3 ppm due to methyl carbons and at 205.0 ppm due to the cationic carbons (Figure 1), indicating that **11** has a symmetrical structure (Scheme 5). The addition of allyltrimethylsilane to the solution gave rise to the formation of diallylated compound **12** in 80% yield.

The reaction with methylmagnesium bromide and a ketene silyl acetal afforded **13** and **14**, respectively, as a mixture of stereoisomers. It is important to note that the anodic oxidation of **15** ($E_{ox} = 1.86$ V, 5.0 F/mol) followed by the reaction with the ketene silyl acetal gave only a trace amount of **14** (ca. 5% yield) together with the monoalkylation product **16** (30% yield), indicating that the dissociation of two C−H bonds to generate dication **11** did not take place effectively. This observation demonstrates the advantage of the present C−C bond dissociation approach to dications. The

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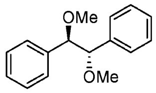
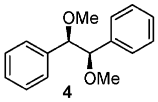
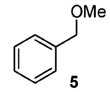
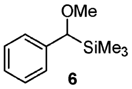
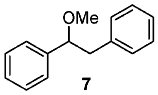
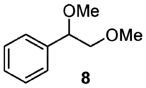
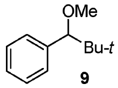
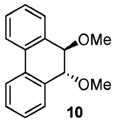
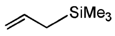
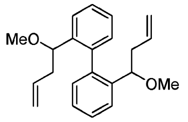
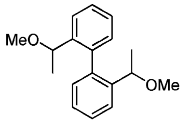
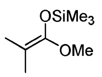
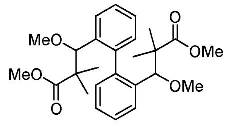
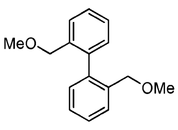
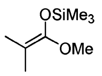
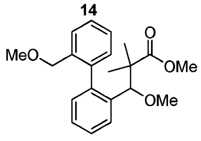
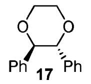
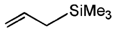
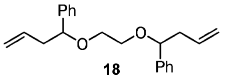
Table 1. Generation of a Pool of **2**[a]

run	substrate	oxidation potential (E_{ox}, V)	temperature (°C)	% yield of **3**[b]
1	 **1**	1.61	−78	47
2			−48	90
3			−25	87
4	 **4**	1.65	−48	79
5	 **5**	2.20	−78	50
6			−48	54
7	 **6**	1.21	−78	73
8	 **7**	1.92	−78	13
9			−48	10
10	 **8**	1.81	−78	42
11			−48	32
12			−25	21
13	 **9**	1.98	−78	49

[a] Reactions were usually carried out with 0.4 mmol of substrate and 2.5 equiv of allyltrimethylsilane. [b] Yields were determined by GC.

Table 2. Generation of Dications and Their Reaction with Nucleophiles[a]

precursor	nucleophile	product	% yield[b,d]
 **10**		 **12**	80 41[c]
	MeMgBr/Et$_2$O	 **13**	74
		 **14**	77
 **15**		 **16**	30
 **17**		 **18**	46 61[e]

[a] Reactions were usually carried out with 0.4 mmol of a precursor. After the electrolysis (2.5 F/mol) at −78 °C, a nucleophile (5.0 equiv) was added at the same temperature. [b] Isolated yields. [c] The electrolysis and the follow-up reaction were carried out at −48 °C. [d] A mixture of isomers. [e] The electrolysis was carried out at −15 °C, and the follow-up reaction was carried out at −78 °C.

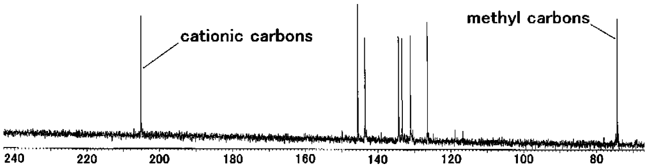


Figure 1. ^{13}C NMR spectrum of **11** (in CD$_2$Cl$_2$, −80 °C).

anodic oxidation of **17** (E_{ox} = 1.45 V) followed by the reaction with allyltrimethylsilane also proceeded smoothly to give the desired diallylated product **18** in good yield. In summary, the present observations illustrate the potential of a new approach for the generation of cation pools, which involves C−C bond dissociation in the radial cation intermediates. It is also noteworthy that the method opens a simple and straightforward approach to dications under mild conditions. Further work is in progress to explore the full range of applicability of the present approach.

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Supporting Information Available: Experimental procedures and analytical and spectroscopic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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