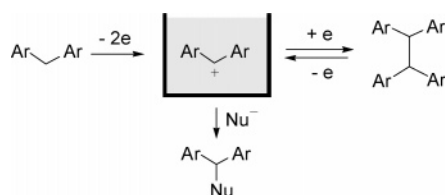# Oxidative Generation of Diarylcarbenium Ion Pools

Masayuki Okajima, Kazuya Soga, Toshiki Nokami, Seiji Suga, and Jun-ichi Yoshida*

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

yoshida@sbchem.kyoto-u.ac.jp

ABSTRACT

"Cation pools" of diarylcarbenium ions have been generated by the oxidative C–H bond dissociation of diarylmethanes using anodic oxidation. "Diarylcarbenium ion pools" thus generated react with various nucleophiles, such as allylsilanes, ketene silyl acetals, and aromatic compounds. The reductive homocoupling of the "diarylcarbenium ion pool" has been achieved. The dimer thus obtained also serves as a precursor of the "diarylcarbenium ion pool" via oxidative C–C bond dissociation.

Diarylcarbenium ions have received significant research interest from a mechanistic viewpoint. Some diarylcarbenium ions are rather stable,[1] and their reactivities toward nucleophiles have been extensively studied.[2] It is also worth noting that diarylcarbenium ions may serve as versatile intermediates for the synthesis of aryl-substituted compounds of interesting functions.

Diarylcarbenium ions are often generated from the corresponding alcohols and halides by ionization in superacid.[1b,3]

Laser flash photolysis has also been utilized as a method for the generation of diarylcarbenium ions.[4] Although some stable diarylcarbenium ions can be prepared using such methods,[5] a general and convenient method for the generation and accumulation of reactive diarylcarbenium ions is still needed.

Recently, we have developed the "cation pool" method that involves irreversible oxidative generation and accumulation of carbocations in the absence of nucleophiles at low temperature.[6] *N*-Acylminium ion pools and alkoxycarbenium ion pools can be easily generated by the oxidative cleavage of C–H, C–Si, and C–C bonds. Thus, it is appropriate to ask if diarylcarbenium ions can be generated by the "cation pool" method. We report herein that the idea works. This is the first example of the generation of "cation pools" without

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having an adjacent cation-stabilizing heteroatom such as oxygen and nitrogen.

The anodic oxidation reactions of various diarylmethanes **1** in Bu$_4$NBF$_4$/CH$_2$Cl$_2$ were carried out using a carbon felt anode, and the resulting solutions were allowed to react with allyltrimethylsilane to obtain the corresponding allylated diarylmethane **5** (Scheme 1).

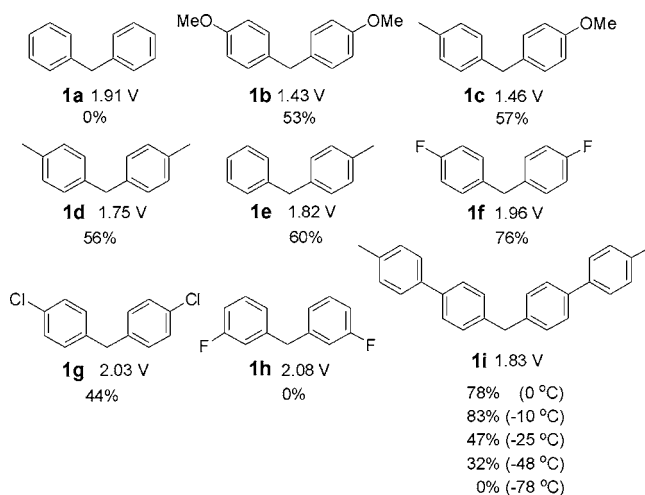**Scheme 1.** Proposed Mechanism of Generation of Diarylcarbenium Ion
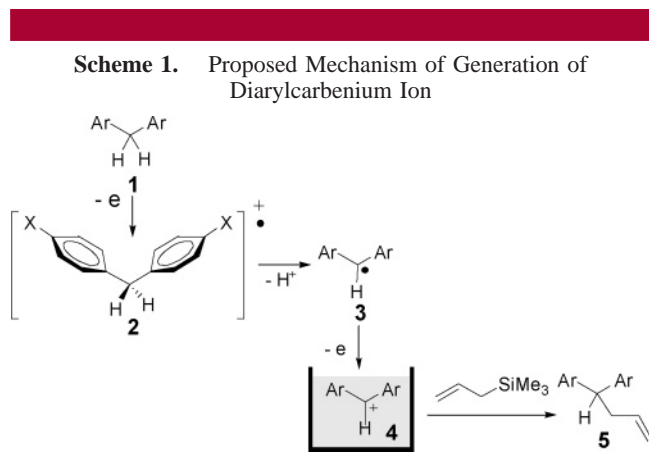
As depicted in Figure 1, the efficiency of the reaction strongly depends on the nature of the diarylmethane. It was surprising that simple diphenylmethane (**1a**) gave complex mixture, and the allylated compound **5a** was not detected, although the detailed mechanism is not clear at present. The introduction of substituents at para positions of the benzene rings resulted in a smooth transformation (**1b**−**g**). Meta substituents did not work (**1h**), and 84% of **1h** was recovered unchanged. Not only electron-donating substituents (**1b**−**e**), but also weak electron-withdrawing substituents (**1f**−**g**) were effective. It is interesting that the introduction of a para substituent on only one of the two phenyl rings is effective for the success of the reaction (**1e**). Successful reaction of extended diarylmethane **1i**, which implies the possibility for the synthesis of various extended π-electron systems, is also worth noting. Easy access to diarylmethanes[7] is an advantage of the present process from a synthetic point of view.

As to the mechanism, Kochi reported that the initial electron transfer from di(pentamethylphenyl)methane leads to the formation of the radical cation localized on a single aromatic ring, which is converted to the radical cation π-delocalized on two aromatic rings.[8] In the present cases,

Figure 1. Oxidation potentials of diarylmethanes **1** and yields of allylated diarylmethanes **5**. Oxidation potentials were determined by RDE (rotating disk electrode) in LiClO$_4$/CH$_3$CN using an SCE as a reference electrode. The electrochemical oxidation was carried out in a divided cell equipped with a carbon felt anode in 0.3 M Bu$_4$NBF$_4$/CH$_2$Cl$_2$ at −78 °C unless otherwise stated under constant current conditions. After the electrolysis (2.5 F/mol), the resulting solution was allowed to react with allyltrimethylsilane at −78 °C for 20 min. Yields of allylated product from **1i** under various temperatures were determined by NMR.

similar processes may take place to generate **2** (Scheme 1). It is well-known that the benzylic C−H bond in such a radical cation is readily cleaved.[9] The overlap of C−H σ orbital with the SOMO of the aromatic ring weakens the C−H bond,[10] which eventually leads to its cleavage to generate benzylic radical **3**. Another important factor is the nature of the substituent on the aromatic ring.[11] An electron-donating group stabilizes the radical cation to suppress the C−H bond cleavage. On the other hand, an electron-withdrawing group facilitates the C−H bond cleavage, although the first electron transfer is less favorable. Experimental results indicate that the electronic nature of the substituent is not so important for the success of the reaction. Anyway, thus-generated carbon radical **3** is further oxidized to give the corresponding diarylcarbenium ion **4** (Scheme 1).[12]

Temperature effect for the reaction of **1i** is interesting (Figure 1). The reaction at −78 °C did not afford the allylated product **5i** at all, and 64% of **1i** was recovered unchanged.

(6) (a) Yoshida, J.; Suga, S.; Suzuki, S.; Kinomura, N.; Yamamoto, A.; Fujiwara, K. *J. Am. Chem. Soc.* **1999**, *121*, 9546. (b) Suga, S.; Suzuki, S.; Yamamoto, A.; Yoshida, J. *J. Am. Chem. Soc.* **2000**, *122*, 10244. (c) Suga, S.; Okajima, M.; Yoshida, J. *Tetrahedron Lett.* **2001**, *42*, 2173. (d) Suga, S.; Okajima, M.; Fujiwara, K.; Yoshida, J. *J. Am. Chem. Soc.* **2001**, *123*, 7941. (e) Suga, S.; Suzuki, S.; Yoshida, J. *J. Am. Chem. Soc.* **2002**, *124*, 30. (f) Yoshida, J.; Suga, S. *Chem. Eur. J.* **2002**, *8*, 2650. (g) Suga, S.; Watanabe, M.; Yoshida, J. *J. Am. Chem. Soc.* **2002**, *124*, 14824. (h) Suga, S.; Suzuki, S.; Maruyama, T.; Yoshida, J. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1545. (i) Suga, S.; Nishida, T.; Yamada, D.; Nagaki, A.; Yoshida, J. *J. Am. Chem. Soc.* **2004**, *126*, 14338. (j) Maruyama, T.; Suga, S.; Yoshida, J. *J. Am. Chem. Soc.* **2005**, *127*, 7324. (k) Okajima, M.; Suga, S.; Itami, K.; Yoshida, J. *J. Am. Chem. Soc.* **2005**, *127*, 6930.

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(10) Bond dissociation energies of radical cations have been studied extensively. Zhang, X.; Bordwell, G. *J. Org. Chem.* **1992**, *57*, 4163.

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(12) The oxidation potentials of radicals have been studied. Wayner, D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.

With the increase of the electrolysis temperature, the yield increased. It seems to be reasonable to consider that the deprotonation of the initially formed radical cation **2i** requires higher temperature because the charge may be delocalized through the extended π-system.

The accumulation of diarylcarbenium ion was confirmed by NMR spectroscopy. For example, a solution of **4f** generated from **1f** exhibited a signal at 192.6 ppm due the carbenium carbon. This chemical shift is very close to that (193.3 ppm) of **4f** generated in a superacid media (SO_2ClF).[13] CSI-MS analysis (spray temperature: -20 °C) also supported the formation of **4f** ($m/z = 203$).

In order to demonstrate the synthetic utility of diarylcarbenium ion pools, several transformations have been examined. As exemplified in Scheme 2, the dicarylcarbenium ion
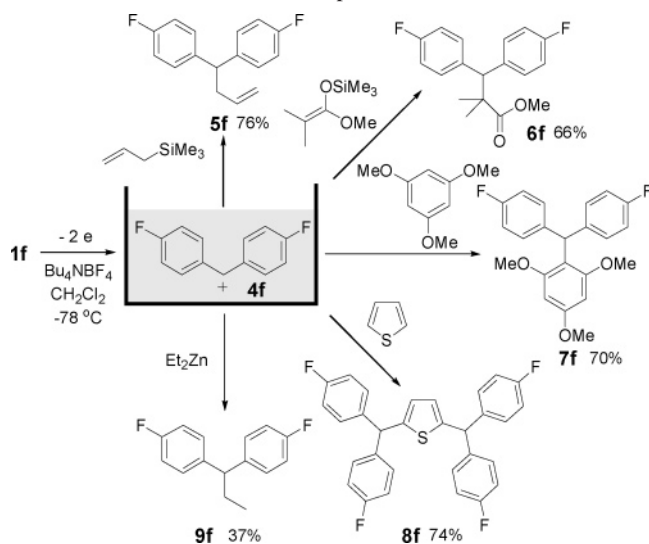
pool **4f** reacted with various nucleophiles including allylsilanes and ketene silyl acetals. Friedel−Crafts-type reactions with aromatic and heteroatomatic compounds also took place smoothly. Such reactions serve as powerful tools for construction of various organic compounds containing aromatic rings. When diethylzinc was used as a nucleophile, the yield of product was not high.

(13) Kelly, D. P.; Jenkins, M. J. *J. Org. Chem.* **1984**, *49*, 409.

Another important transformation of the diarylcarbenium ion pool is reductive homocoupling (Scheme 3). For example,

Scheme 3. Reductive Homocoupling of Diarylcarbenium Ion and Oxidative Cleavage of Tetraarylethane
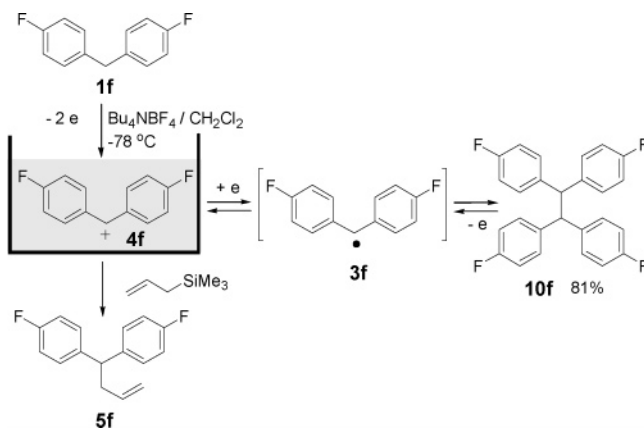
1f was anodically oxidized at -78 °C to generate **4f**, and the resulting solution was cathodically reduced at -78 °C. The homocoupling product **10f** was obtained in 81% yield, presumably via radical **3f**.[14] It should be noted that the reverse transformation can also be accomplished electrochemically. The anodic oxidation of **10f** at -78 °C generated **4f** via oxidative C−C bond dissociation,[6k] which can be trapped by allyltrimethylsilane to give **5f** (55% yield).

In summary, the "cation pool" method was found to be effective for the generation of diarylcarbenium ions, although the efficiency depends on the nature of the starting diarylmethanes. The present method serves as powerful tools for the construction of various organic compounds having diarylmethane structures. Further work is in progress to explore the scope and limitations of the present method and to develop its applications to the synthesis of organic architectures containing aromatic rings.

Supporting Information Available: Experimental procedures and characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OL061647C

(14) Reductive coupling of "cation pool": Suga, S.; Suzuki, S.; Maruyama, T.; Yoshida, J. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1545. See also ref 6e.