

Electrochemical Generation of Diarylcarbenium Ions and their Reactions with Aromatic Compounds.

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Diarylcarbenium ions have received significant research interest from a mechanistic and a synthetic view points. Some diarylcarbenium ions are rather stable and their reactivity toward nucleophiles has been extensively studied. It is also noteworthy 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 super acid. Laser-flash photolysis has also been utilized as a method for the generation of diarylcarbenium ions, although, to the best of our knowledge, the generation of diarylcarbenium ions by electrochemical methods had never been examined when we initiated this study.

We have developed the "cation pool" method that involves irreversible oxidative generation and accumulation of carbocations in the absence of nucleophiles at low temperature. *N*-Acylminium ion pools and alkoxy-carbenium ion pools can be easily generated by the oxidative cleavage of C-H, C-Si, and C-C bonds. Diarylcarbenium ions are found to be generated by the "cation pool" method¹ and we applied for dendrimer synthesis.² During the course of our study, we also found that generation efficiency of diarylcarbenium ions highly depends on diarylmethanes and high reactivity of electrochemically generated diarylcarbenium ions. Here we report the detail of our findings about the "cation pool" of diarylcarbenium ions.

We initiated our study by measuring the oxidation potential of diphenylmethane derivatives. As shown in Table 1, oxidation potentials of diphenylmethane derivatives were lower than 2 V. These values indicated that all these molecules can be oxidized under conventional preparative electrochemical conditions. The low-temperature anodic oxidation of diphenylmethane derivatives was performed under the "cation pool" condition and thus-generated cations were treated with allyltrimethylsilane as a nucleophile (Table 1). When we used *p*-difluorodiphenylmethane **1a** as a precursor of the diarylcarbenium ion, the allylated product **3a** was obtained in reasonable yield (76%). On the other hand, diphenylmethane **1b** did not give the corresponding allylated product **3b** and the significant amount (54%) of diphenylmethane **1b** was recovered (entry 2). The anodic oxidation of fluorene **1c** seems to be interesting because fluorenyl cation might be anti-aromatic. Though **1c** was consumed completely during the electrolysis, the allylated product **3c** was not obtained after treatment with allyltrimethylsilane (entry 3). 9,10-Dihydroanthracene **1d** gave the allylated product **3d** in 80% yield at -78 °C (entry 4). Xanthene **1e** and dibenzosuberane **1f** gave allylated products **3e** and **3f** in reasonable yields at higher temperature (-48 °C) (entries 5 and 6). In both cases, yields of allylated products were moderate at -78 °C as shown in parentheses.

High reactivity of *p*-difluorodiphenylcarbenium ion **2a** inspired us to investigate multi-addition toward

Table 1.

entry	substrate	Eox	temperature	product/yield
1		1.96 V	-78 °C	3a 76%
2		1.91 V	-78 °C	3b 0%
3		1.52 V	-78 °C	3c 0%
4		1.44 V	-78 °C	3d 80%
5		1.36 V	-48 °C	3e 70% (38%) ^a
6		1.91 V	-48 °C	3f 71% (17%) ^a

^aReactions were performed at -78 °C.

aromatic compounds. For example, the Friedel-Crafts type reaction of diarylcarbenium ions **2a** with thiophene afforded the tri-adduct **4** in low yield (32%). Thus, we also examined 3,3'-bithiophene and 1,3,5-tri(3'-thienyl)-benzene as nucleophiles. The multi-addition of diarylcarbenium ions **2a** toward these nucleophiles afforded tetra-adduct **5** and hexa-adduct **6** in moderate yields (49% and 76%).

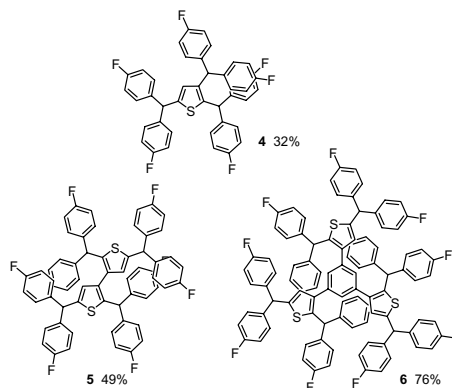


Figure 1.

References

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- Nokami, T.; Ohata, K.; Inoue, M.; Tsuyama, H.; Shibuya, A.; Okajima, M.; Soga, K.; Suga, S.; Yoshida, J. *J. Am. Chem. Soc.* **2008**, *130*, 10864.