Tetrahedron 67 (2011) 4664–4671

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Electrochemical synthesis of dendritic diarylcarbenium ion pools

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ARTICLE INFO

Article history:
Received 8 March 2011
Received in revised form 8 April 2011
Accepted 14 April 2011
Available online 27 April 2011

Keywords:
Dendrimer
Carbocation
Electrochemical oxidation
Friedel–Crafts alkylation

ABSTRACT

Dendritic diarylcarbenium ion pools were synthesized by the low temperature electrochemical oxidation of the corresponding dendritic (diarylmethyl)trimethylsilanes, which were prepared by use of the iterative method consisting of electrochemical activation and Friedel–Crafts type coupling. Time-course NMR studies revealed that thermal stability of dendritic diarylcarbenium ions depends both on the generation of the dendritic structure and on the *para*-substituents of the terminal phenyl groups. Dendritic diarylcarbenium ions up to the third generation exhibited high reactivity as a carbon electrophile.

1. Introduction

Organic cations (carbocations and onium ions) are important reactive intermediates in organic synthesis.[1] It is noteworthy that the manner in which we carry out reactions of organic cations is different from that for carbanions. Usually, organic cations are produced in the presence of nucleophiles to achieve a desired transformation. In contrast, carbanions are produced and accumulated in a solution in the absence of electrophiles, and an electrophile is added to the solution of the pre-formed carbanion. This is probably because organic cations that are often used in organic synthesis are unstable and transient in conventional reaction media and should be trapped in situ by nucleophiles immediately after their preparation. In this context, development of a new method that enables production and accumulation of organic cations in the absence of nucleophiles is strongly needed for expanding the scope of cation chemistry in organic synthesis. In 1999 we have developed the 'cation pool' method,[2] whereby organic cations are produced in the absence of nucleophiles and are used for the subsequent reactions (Fig. 1). Various organic cation including *N*-acyliminium ions and alkoxycarbenium ions can be produced and accumulated as 'cation pools'.

The 'cation pool' method is based on the irreversible oxidative production of organic cations. In the first step, a cation precursor is electrochemically[3] oxidized to produce and accumulate an organic cation in the solution in the absence of a nucleophile. To avoid thermal decomposition of the cation, the electrolysis should be carried out at low temperatures, such as −78 °C. Counter anions, which are considered to be very weak nucleophiles, such as BF_4^- are normally used to prevent the nucleophilic attack on the cationic center. After electrolysis is complete, a nucleophile is then added to obtain the desired product. The 'cation pool' method serves as a flexible way of using organic cations in organic synthesis in comparison with the conventional in situ preparation method. It is also important to note that the 'cation pool' method is applicable to spectroscopic characterization and studies on stability and reactivity of unstable organic cations.

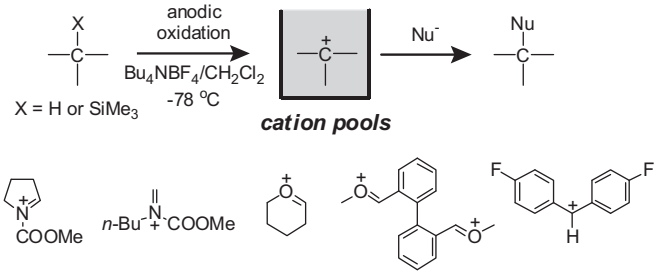

Fig. 1. The general scheme of the 'cation pool' method and some examples of organic cations, which have been produced and accumulated as 'cation pools'.

Recently, we developed an iterative process based on the 'cation pool' method, which consists of a sequence of synthesis of a diarylcarbenium ion pool[4] followed by coupling with (diphenylmethyl)trimethylsilane as a building block (Fig. 2).[5] The process enables convergent synthesis of dendritic molecules.[6] During the course of this study, we have produced and accumulated dendritic

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doi:10.1016/j.tet.2011.04.065

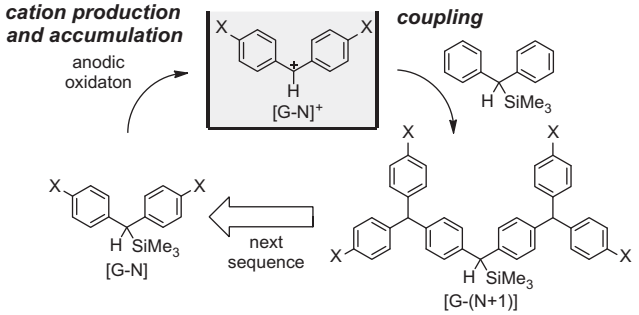
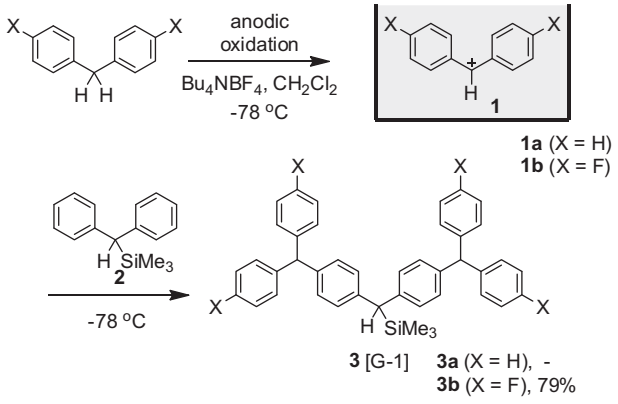


Fig. 2. An iterative process based on the sequential synthesis of diarylcarbenium ions and coupling with (diphenylmethyl)trimethylsilane.

diarylcarbenium ions in the solution. To the best of our knowledge, structures, stability, and reactivity of such large-size organic cations have not been studied comprehensively.[7] In this article, we report the full details of our studies on synthesis, characterization, and thermal stability of dendritic diarylcarbenium ion pools.

2. Results and discussion

We initiated our study by synthesizing precursors of the first generation dendritic diarylcarbenium ion pools. Although it was difficult to produce diphenylcarbenium ion (**1a**) from diphenylmethane by the cation pool method,[2o] the low temperature electrochemical oxidation of di(*p*-fluorophenyl)methane in Bu_4NBF_4/CH_2Cl_2 using an H-type divided cell at −78 °C (3.0 F/mol) gave a pool of di(*p*-fluorophenyl)carbenium ion (**1b**), which was allowed to react with (diphenylmethyl)trimethylsilane (**2**) to give the organosilicon precursor **3b** [G-1] in 79% yield (Scheme 1).[8] The structure of **3b** was confirmed by the X-ray crystal analysis. An ORTEP diagram of **3b** is shown in Fig. 3.



Scheme 1. Preparation of precursors of the first generation of dendritic diarylcarbenium ions **3** [G-1].

Choice of a building block was important to construct dendritic structure having the triarylmethane repeating unit. It was reported that the introduction of a silyl group at the benzylic position increases the HOMO level of the benzene ring to enhance its reactivity.[9] The interaction of the C–Si σ-orbital with the π-orbital of the benzene is responsible. In fact, the oxidation potential of **2** is much lower than that of diphenylmethane (Fig. 4). It is also known that if the outer-sphere electron transfer takes place, the C–Si bond in the resulting radical cation is readily cleaved.[10–12] However, Mayr and co-workers reported that the outer-sphere electron transfer is definitely excluded for the reaction of diarylcarbenium ions with nucleophiles.[4f]

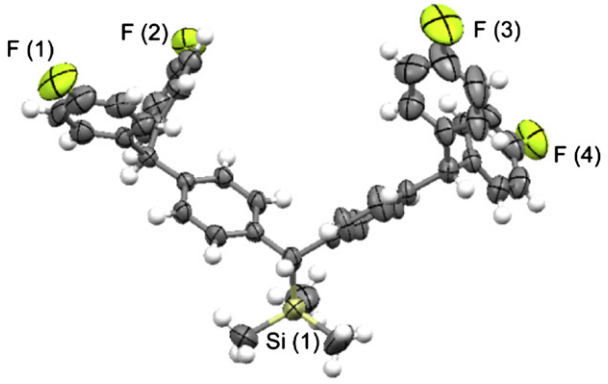


Fig. 3. X-ray structure of **3b**. Thermal ellipsoids are drawn at the 50% probability level.

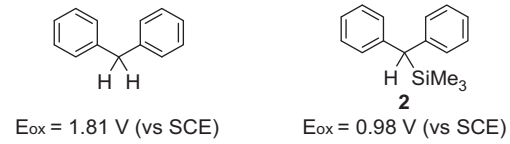
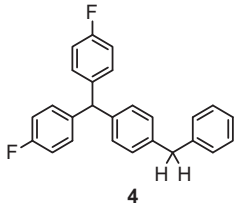
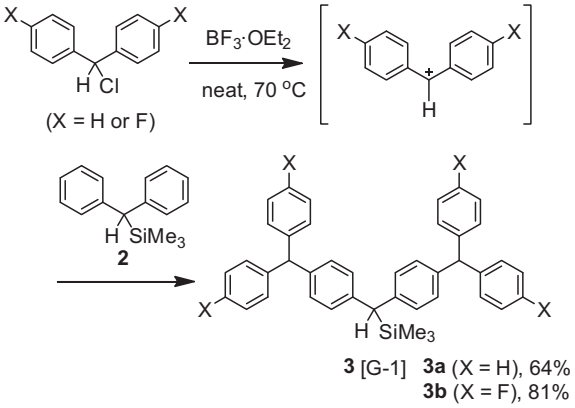


Fig. 4. The oxidation potential of diphenylmethane and (diphenylmethyl)trimethylsilane (**2**).

To confirm the effect of the trimethylsilyl group at the benzylic position on the reactivity, the reaction of **1b** with dipheylmethane was carried out under the same condition. The reaction did not give the disubstituted compound. Instead 1:1 adduct **4** was obtained in very low yield (11%).



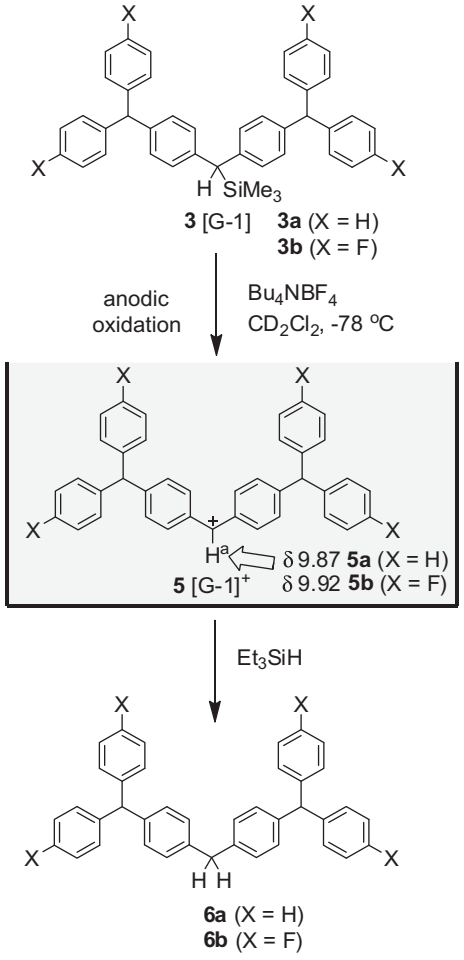
Diarylcarbenium ions **1** were also easily produced in situ by the conventional chemical method using the corresponding diarylmethyl chlorides as precursors (Scheme 2). In this case simple diphenylcarbenium ion **1a** could be produced and used for the reaction with **2**. The reaction of diphenylmethyl chloride with borontrifluoride diethyletherate ($BF_3{\cdot}OEt_2$) in the presence of **2** at



Scheme 2. Preparation of precursors of the first generation of dendritic diarylcarbenium ions **3** [G-1] by the conventional chemical reaction.

70 °C gave **3a** in 64%. Compound **3b** was also prepared by the same method from di(*p*-fluorophenyl)methyl chloride in 81% yield.

Fortunately, the conventional Lewis-acid mediated reactions afforded both organosilicon precursors **3a** and **3b**, which were subsequently used as precursors for producing the first generation dendritic diarylcarbenium ions **5** $[G\text{-}1]^+$ using the 'cation pool' method (Scheme 3). The low temperature electrochemical oxidation of **3a** and **3b** was carried out at −78 °C in Bu_4NBF_4/CD_2Cl_2 to produce **5a** and **5b**, respectively (2.5 F/mol). The resulting anodic solution was quickly transferred to an NMR tube with cold glass syringes. ^1H NMR at −80 °C (Fig. 5) indicated the selective formation **5a** and **5b** by the cleavage of the C–Si bond without affecting benzylic C–H bonds (vide infra). There were two sets of peaks $H^b/H^{b'}$ and $H^c/H^{c'}$, which were assigned as protons of phenyl groups adjacent to the cation carbon. These peaks became time averaged signals above −40 °C due to the free rotation of phenyl groups (See Supplementary data for details). The accumulation of **5a** and **5b** was also confirmed by their reduction with Et_3SiH to give **6a** and **6b**, respectively.



Scheme 3. Preparation of the first generation of dendritic diarylcarbenium ions **5** $[G\text{-}1]^+$ by the 'cation pool' method and the subsequent treatment with triethylsilane.

^1H NMR spectra of the first generation dendritic diarylcarbenium ions did not change during measurements at −80 °C. Thus, the thermal stability of **5a** and **5b** was investigated by the time-course NMR analysis at elevated temperature (Fig. 6). The intensity of the signal of the methine proton (H^a) of **5a** decreased gradually and disappeared completely in 4 h at −20 °C. Decomposition of **5b** was slower even at higher temperatures, such as 0 °C. Decomposition of **5a** led to the formation of oligomeric products, although it was difficult to fully characterize them.

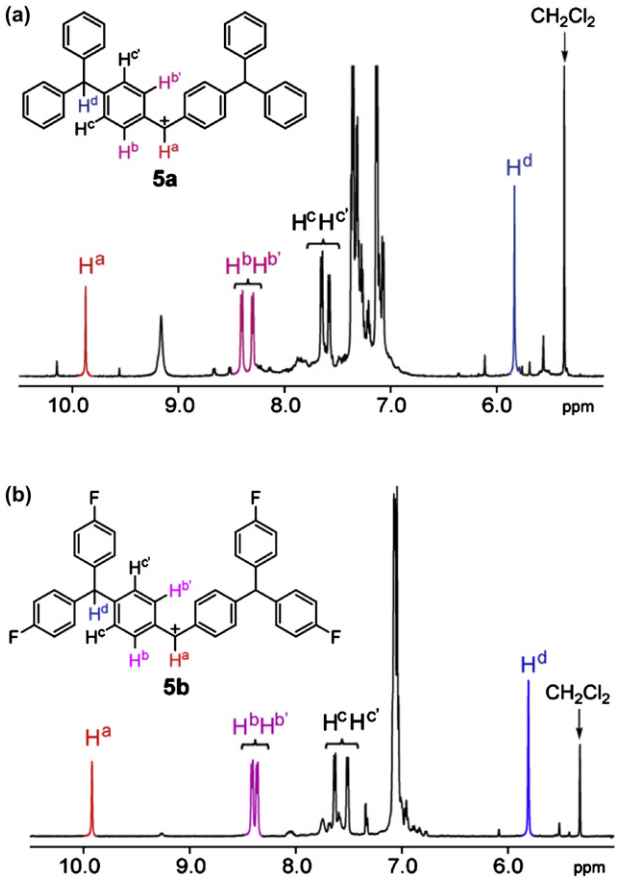


Fig. 5. ^1H NMR spectra of dendritic diarylcarbenium ions **5a** (a) and **5b** (b) at −80 °C.

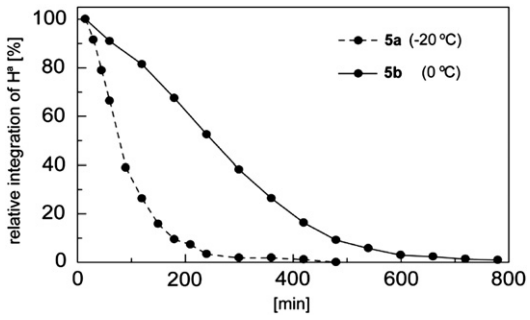
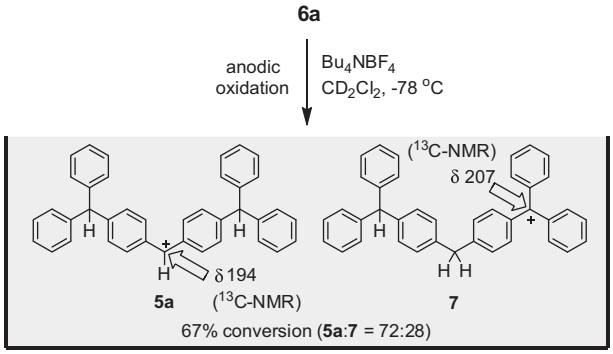


Fig. 6. Decomposition profiles of the first generation of dendritic diarylcarbenium ions **5** $[G\text{-}1]^+$ obtained by time-course NMR analyses (**5a**: at −20 °C and **5b**: at 0 °C) (relative intensity of H^a proton at 15 min).

Presumably the coupling of the cationic carbon of **5a** and the *para*-position of terminal phenyl groups took place to give the oligomers. In the case of **5b**, however, the *para*-positions are substituted by fluorine atoms, and therefore the phenyl groups are less reactive toward the cationic species, making **5b** thermally more stable. Upon decomposition, two signals appeared at around 4 ppm, which are assigned to $ArCH_2Ar$, in ^1H NMR spectrum (See Supplementary data for details). The signal at 3.94 ppm corresponds to **6b**, indicating that simple reduction of **5b** occurred, although the hydride source is not clear at present. The signal at 4.27 ppm seems to indicate the formation of triarylcarbenium ion, which is similar to **7** (Scheme 4), because the chemical shift is very similar. This means that the migration of the cationic center took place, although the mechanism of hydride shift is not clear at present.

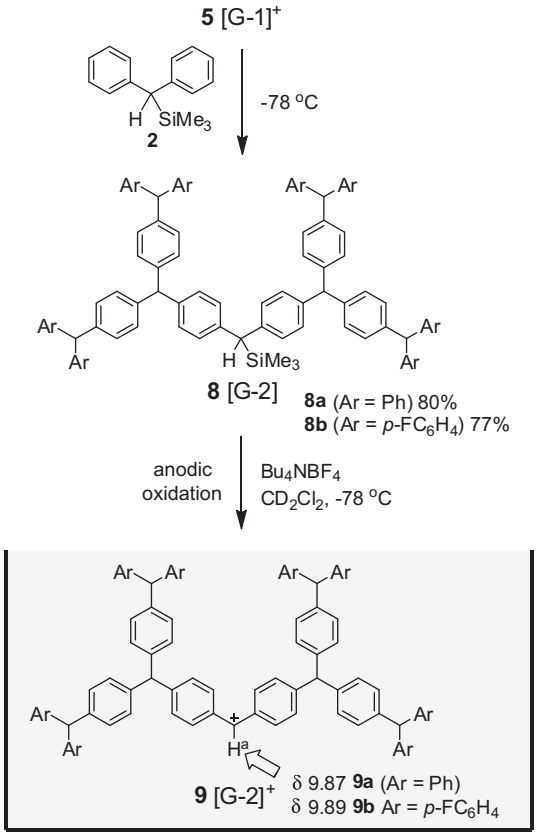
In the preparation of the first generation dendritic diarylcarbenium ions **5a** and **5b**, the effect of the trimethylsilyl (Me_3Si)



Scheme 4. Preparation of the 'cation pool' from compound **6a** as a precursor.

group as an electroauxiliary is remarkable. In fact, the oxidation potential of **3a** (1.26 V vs SCE), which has a Me_3Si group at the carbon bearing two aryl groups, is much lower than that of the corresponding compound without the Me_3Si group (**6a**, 1.73 V vs SCE). It is also noteworthy that the carbon bearing two aryl groups was oxidized selectively without affecting the carbons bearing three aryl groups and that the C–Si bond was cleaved selectively without affecting C–H bonds in the same molecule. In contrast, the electrochemical oxidation of **6a** gave a mixture of **5a** and **7** (72:28); the latter being produced by the oxidation of the carbon bearing three aryl groups (Scheme 4). Therefore, the Me_3Si group acted as an electroauxiliary, which activates substrate molecules toward electron transfer and controls the subsequent chemical process to give the desired cation selectively.[13]

Next, preparation of the second generation dendritic diarylcarbenium ion pools **9** $[G\text{-}2]^+$ was achieved using the same method (Scheme 5). The first generation dendritic diarylcarbenium ions **5** were allowed to react with **2** to obtain the corresponding precursors **8** in reasonable yields.[14] The low-temperature electrochemical oxidation of **8a** and **8b** afforded the 'cation pools' of **9a** and **9b**, respectively, which were also characterized by low-temperature ^1H and ^{13}C NMR analyses.



Scheme 5. Preparation of the second generation of dendritic diarylcarbenium ion pools **9** $[G\text{-}2]^+$ by the 'cation pool' method.

The thermal stability of **9a** and **9b** was investigated by the time-course NMR measurements. As shown in Fig. 7, **9b** decomposed slower than **9a**, presumably because fluorine substituents at the *para*-positions in **9b** suppress the coupling of the cationic carbon and terminal phenyl groups. The significant difference in thermal stability between the first generation and the second generation is interesting. The second generation dendritic diarylcarbenium ion **9a** is less stable than the first generation **5a**. In fact, **9a** decomposed completely in 1.5 h at −20 °C, whereas it took 3.5 h for **5a** to decompose at the same temperature. Similarly, it took 3.5 h for **9b** to decompose completely at 0 °C, whereas it took 10 h for **5b** to decompose at the same temperature. Upon decomposition, several signals appeared at around 4 ppm, which are assigned to $ArCH_2Ar$, in ^1H NMR spectrum (See Supplementary data for details). Presumably, both simple reduction and migration of the cationic center took place, although the details are not clear at present.

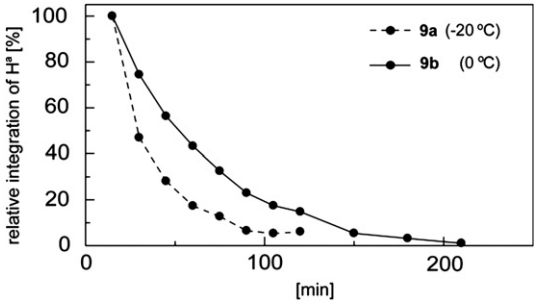
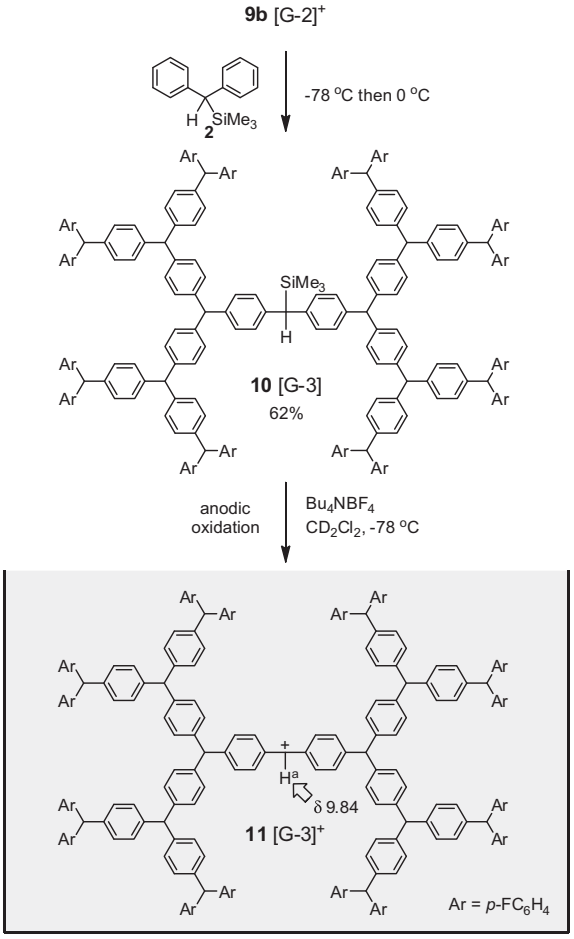


Fig. 7. Decomposition profiles (relative intensity of H^a proton at 15 min) of the first and the second generation of dendritic diarylcarbenium ions **9a** and **9b** obtained by time-course NMR analyses.

The third generation dendritic diarylcarbenium ion was prepared in the similar manner (Scheme 6). Because of better thermal stability, we focused on the fluorine-substituted dendritic diarylcarbenium ions. The precursor **10** [G-3] was prepared by the reaction of **9b** with **2** at 0 °C in 62% yield,[15] and was oxidized electrochemically to synthesize the cation pool of **11** $[G\text{-}3]^+$, which was characterized by the low-temperature NMR spectroscopy. ^1H NMR spectrum indicated the complete conversion of **10** and the formation of **11** as a single species. A signal observed at δ 9.84 (singlet) was assigned to the proton adjacent to the cationic carbon. Several attempts to observe the cationic carbon of **11** by the ^{13}C NMR were failed, although the reason is not clear at present.

The thermal stability of **11** $[G\text{-}3]^+$ was also investigated by the time-course NMR measurements and was compared with those of lower generation dendritic diarylcarbenium ions **5b** $[G\text{-}1]^+$ and **9b** $[G\text{-}2]^+$. As shown in Fig. 8, **11** decomposed faster than **9b** and **5b**, indicating that the thermal stability of the dendritic diarylcarbenium ions decreases with an increase in the generation of the dendritic structure. Although the reason for the tendency has not yet been fully clarified, it seems to be reasonable from ^1H NMR spectra of decomposition products (See Supplementary data for details) to consider that migration of the cationic center is one of the major pathways of decomposition of the dendritic diarylcarbenium ions. Thus, we assume that rapid migration of the cationic center is responsible for faster decomposition of the higher generation of dendritic diarylcarbenium ions because the number of the triarylmethyl moiety is greater than that in the lower generations.



Scheme 6. Preparation of the third generation of dendritic diarylcarbenium ions **11** $[G\text{-}3]^+$ by the 'cation pool' method.

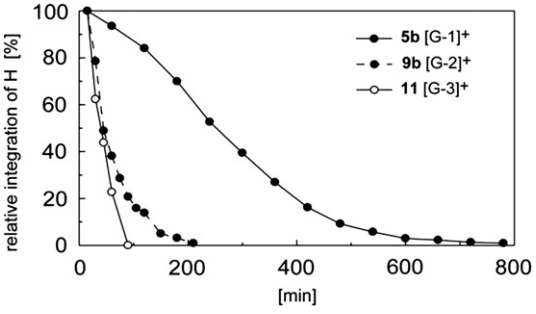
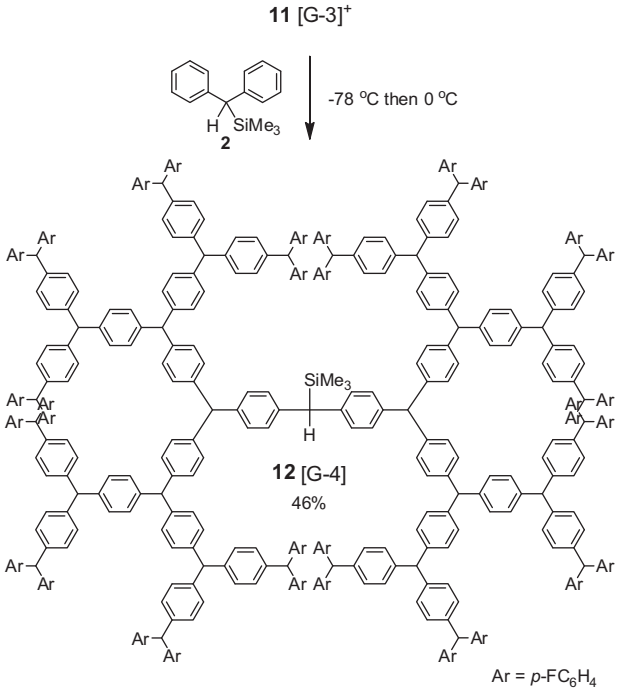


Fig. 8. Decomposition profiles (relative intensity of H^a proton in 15 min) of the first (**5b**), the second (**9b**), and third (**11**) generation of dendritic diarylcarbenium ions obtained by time-course NMR analyses at 0 °C.

Finally, the production and accumulation of **11** $[G\text{-}3]^+$ was also confirmed by the reaction with **2**, which gave the corresponding 2:1 adduct **12** [G-4] in 46% yield, although the yield was not optimized (FAB-MS: *m*/*z* calcd for $C_{406}H_{288}F_{32}AgSi$ $[M+Ag^+]$: 5905.0840, found: 5905.0845) (Scheme 7). This result clearly showed that selective activation of carbon–silicon bond occurred with such a huge organosilicon compound **10** and the third generation dendritic diarylcarbenium ion **11** has reasonble reactivity as an electrophile.

3. Conclusion

In conclusion, we have developed a new method for producing and accumulating dendritic diarylcarbenium ions up to the third generation in the solution based on the 'cation pool' method. The dendritic diarylcarbenium ions that are reactive as an electrophile have sufficient stability to characterize in detail by NMR analyses at low temperature. We believe that these findings open a new possibility of carbocation chemistry, organic electrochemistry, and dendrimer synthesis. Scope and limitations of functional groups and further applications including the dendronized polymer synthesis, taking advantage of high reactivity of dendritic diarylcarbenium ions, are currently in progress in our laboratory.



Scheme 7. Reaction of the third generation of dendritic diarylcarbenium ions **11** $[G\text{-}3]^+$ with diphenylmethyltrimethylsilane.

4. Experimental section

4.1. General

^1H and ^{13}C NMR spectra were recorded on JEOL ECA-600P (^1H 600 MHz, ^{13}C 150 MHz). Chemical shifts are reported using the methine signal of $CHCl_3$ at δ 7.26 (^1H NMR) and δ 77.0 (^{13}C NMR) as internal standards. FAB mass spectra were recorded on JEOL JMS-HX110A spectrometer. IR spectra were recorded on Shimadzu IRAffinity-1 FT-IR spectrophotometer equipped with MIRacle ATR sampling accessory. Melting points were measured on Electrothermal Mel-Temp manual melting point apparatus. Preparative gel permeation chromatography was performed on Japan Analytical Industry LC-918 (an eluent: $CHCl_3$). X-ray single crystal structure analysis was performed on RIGAKU R-AXIS RAPID. Dichloromethane was washed with water, distilled from P_2O_5, redistilled from dried K_2CO_3 to remove a trace amount of acid, and stored over molecular sieves 4A. Compounds and cation species **3b**, **4**, **5b**, **8b**, **9b**, and **10** have already reported in the previous communication.[5] Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification.

4.2. Preparation of the first generation dendritic organosilicon compounds

4.2.1. The electrochemical method. The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon

felt anode (Nippon Carbon JF-20-P7, ca. 160 mg, dried at 250 °C/1 mmHg for 2.5 h before use) and a platinum plate cathode (20 mm×10 mm). In the anodic chamber were placed a solution of 4,4′-difluorodiphenylmethane (75.1 mg, 0.368 mmol) and 0.3 M Bu_4NBF_4/CH_2Cl_2 (8.0 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (64 μL, 0.72 mmol) and 0.3 M Bu_4NBF_4/CH_2Cl_2 (8.0 mL). The constant current electrolysis (12.0 mA) was carried out at −78 °C with magnetic stirring until 3.0 F/mol of electricity was consumed. Then (diphenylmethyl)trimethylsilane (36.2 mg, 0.151 mmol) was added to the anodic chamber at −78 °C and the mixture was stirred for 20 min. The resulting mixture was treated with triethylamine (0.3 mL) at −78 °C. After stirring at room temperature for 10 min, the solvent was removed under reduced pressure and the residue was quickly filtered through a short column (2×3 cm) of silica gel to remove Bu_4NBF_4 by using hexane/AcOEt=1/1 as an eluent. Removal of the solvent of the combined filtrate under reduced pressure and the crude product thus-obtained was purified with flash chromatography to obtain **3b** as a colorless crystal in 79% yield (NMR yield). *Bis*(4-*bis*(4-*fluorophenyl*)*methyl-phenyl*)*methyl-trimethylsilane* (**3b**). Mp 125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–7.18 (m, 4H), 7.07–7.04 (m, 8H), 7.00–6.96 (m, 12H), 5.48 (s, 2H), 3.50 (s, 1H), 0.05 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, *J*=236.5 Hz), 140.8, 140.0, 139.5 (d, *J*=2.8 Hz), 130.6 (d, *J*=7.9 Hz), 128.9, 128.5, 115.0 (d, *J*=21.1 Hz), 54.9, 45.4, −1.5. HRMS (FAB) *m*/*z* calcd for $C_{42}H_{36}F_4Si$: 644.2522, found 644.2523. IR (cm^{-1}): 2955, 1601, 1504, 1223, 1157. X-ray data for **3b**: $C_{42}H_{36}F_4Si$, *M*=644.80, triclinic, space group *P*−1 (No. 2), *a*=10.9102(4) Å, *b*=11.5590(4) Å, *c*=14.7982(5) Å, β=77.4670(10), *V*=1744.86(11) Å^3, *Z*=2, D_c=1.227 g/cm^3, μ=1.17 cm^{-1}. Intensity data were measured on a Rigaku R-AXIS imaging plate area detector with graphite-monochromated Mo Kα radiation. The data were collected at 100±1 K to maximum 2θ value of 27.5°. A total of 17,196 reflections were collected. The structure was solved by SHELX-97[16] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined by using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 7912 observed reflections ($I>2.00\sigma(I)$) and 460 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of *R*=0.041 (R_w=0.149). GOF=1.11, CCDC-802918. All calculations were performed using the Yadokari-XG crystallographic software package.[17]

(4-*Bis*(4-*fluorophenyl*)*methylphenyl*)*phenylmethane* (**4**). Synthesis of the diarylcarbenium ion pool **1** from 4,4′-difluorodiphenylmethane (78.1 mg, 0.38 mmol) and its reaction with diphenylmethane (28.9 mg, 0.17 mmol) afforded a mixture of **4** (7.0 mg, 0.021 mmol) as a colorless oil in 11% yield (isolated yield by preparative GPC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.27 (m, 2H), 7.22–7.19 (m, 3H), 7.13–7.11 (d, *J*=8.0 Hz, 2H), 7.06–7.03 (m, 4H), 7.00–6.95 (m, 6H), 5.47 (s, 1H), 3.96 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (d, *J*=243.6 Hz), 141.2, 140.9, 139.5 (d, *J*=3.2 Hz), 139.4, 130.7 (d, *J*=7.9 Hz), 129.3, 129.0, 128.5, 126.1, 115.1 (d, *J*=21.0 Hz), 54.9, 41.5. HRMS (FAB) *m*/*z* calcd for $C_{26}H_{20}F_2$: 370.1533, found 370.1531. IR (cm^{-1}): 3028, 1601, 1504, 1223, 1157.

4.2.2. The conventional chemical method. Chlorodiphenylmethane (10.0 g, 10.4 mmol), (diphenylmethyl)trimethylsilane (0.95 g, 3.94 mmol) were dissolved in $BF_3\cdot OEt_2$ (2.84 g, 20.0 mmol). After stirring at 70 °C for 12 h, the reaction was treated with ice water and extracted with AcOEt and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified with flash chromatography and GPC to obtain **3a** as a white solid in 64% yield (1.45 g, 2.53 mmol). *Bis*(4-*bis*(*phenyl*)*methylphenyl*)-*methyltrimethylsilane* (**3a**). Mp 120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.25 (m, 8H), 7.22–7.18 (m, 4H), 7.15–7.10 (m, 12H), 6.98 (d, 4H), 5.49 (s, 2H), 3.45 (s, 1H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.14, 144.13, 140.7, 140.3, 129.4, 129.2, 128.5, 128.2, 126.2, 56.4, 45.2, −1.7. HRMS (FAB) *m*/*z* calcd for $C_{42}H_{40}Si$: 572.2899, found 572.908. IR (cm^{-1}): 3024, 1597, 1492, 1447, 1246. *Bis*(4-*bis*(4-*fluorophenyl*)*methyl-phenyl*)-*methyltrimethylsilane* (**3b**). The reaction of chlorobis(4-fluorophenyl) methane (10.0 g, 42 mmol) and trimethylsilyl-diphenyl methane (3.99 g, 16.6 mmol) in $BF_3\cdot OEt_2$ afforded a mixture of **3b** (8.59 g, 13.3 mmol) in 80% yield (isolated yield by flash chromatography and precipitation from methanol).

4.3. The low-temperature and the time-course NMR analyses of the first generation of dendritic diarylcarbenium ions

4.3.1. NMR analysis of the first generation of dendritic diarylcarbenium ions. The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon GF-20-P21E, ca. 160 mg, dried at 250 °C/1 mmHg for 2.5 h before use) and a platinum plate cathode (10 mm×10 mm). In the anodic chamber were placed **3a** (115 mg, 0.20 mmol) and 0.3 M Bu_4NBF_4 in CD_2Cl_2 (5.0 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (35 μl, 0.40 mmol) and 0.3 M Bu_4NBF_4 in CD_2Cl_2 (5.0 mL). The constant current electrolysis (5.0 mA) was carried out at −78 °C with magnetic stirring. After 2.5 F/mol of electricity was consumed, an aliquot of the anodic solution was transferred to a 5 mm ϕ NMR tube with a septum cap under Ar atmosphere at −78 °C. The NMR measurement was carried out at −80 °C. Chemical shifts were reported using signals of CH_2Cl_2 at 5.32 ppm (^{1}H NMR) and CD_2Cl_2 at 53.8 ppm (^{13}C NMR) as standards. Selected data for the first generation of dendritic diarylcarbenium ion **5a**; ^{1}H NMR (600 MHz, CD_2Cl_2) δ 9.87 (s, 1H), 8.38 (d, *J*=8.2 Hz, 2H), 8.28 (d, *J*=8.3 Hz, 2H), 7.63 (d, *J*=8.2 Hz, 2H), 7.56 (d, *J*=8.2 Hz, 2H), 7.35–7.04 (m), 5.79 (s, 2H). ^{13}C NMR (150 MHz, CD_2Cl_2) δ 194.0 (cationic carbon).

The anodic oxidation of **3b** (208 mg, 0.32 mmol) afforded **5b**. Selected peaks for **5b**, ^{1}H NMR (600 MHz, CD_2Cl_2) δ 9.87 (s, 1H), 8.37 (d, *J*=7.6 Hz, 2H), 8.31 (d, *J*=6.2 Hz, 2H), 7.63 (d, *J*=8.2 Hz, 2H), 7.51 (d, *J*=6.9 Hz, 2H), 7.00–6.88 (m), 5.72 (s, 2H), 5.50 (s, 4H). ^{13}C NMR (150 MHz, CD_2Cl_2) δ 194.4 (cationic carbon).

4.3.2. Preparation of the extended diarylmethane. The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca. 160 mg, dried at 250 °C/1 mmHg for 2.5 h before use) and a platinum plate cathode (20 mm×10 mm). In the anodic chamber were placed of bis(4-bis(phenyl)methyl-phenyl)methyltrimethylsilane **3a** (229.0 mg, 0.400 mmol) and 0.3 M Bu_4NBF_4/CH_2Cl_2 (9.0 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (70 μL, 0.79 mmol) and 0.3 M Bu_4NBF_4/CH_2Cl_2 (9.0 mL). The constant current electrolysis (9.0 mA) was carried out at −78 °C with magnetic stirring until 2.5 F/mol of electricity was consumed. Then triethylsilane (121.0 mg, 1.04 mmol) was added to the anodic chamber at −78 °C and the mixture was stirred for 1 h. The resulting mixture was treated with triethylamine (0.2 mL) at −78 °C. After stirring at room temperature for 10 min, the solvent was removed under reduced pressure and the residue was quickly filtered through a silica gel short column to remove Bu_4NBF_4 by using hexane/AcOEt 1:1 as an eluent. Removal of the solvent of the combined filtrate under reduced pressure and the crude product thus-obtained was purified with flash chromatography and GPC to obtain *Bis*(4-*bis*(*phenyl*)*methylphenyl*)*methane* (**6a**) as a pale yellow solid in 54% yield (108 mg, 0.22 mmol). Mp 144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) 7.30–7.24 (m, 10H), 7.23–7.18 (m, 4H), 7.12–7.08 (m, 10H), 7.03–7.00 (m, 4H), 5.50 (s, 2H), 3.92 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) 144.0, 141.6, 139.0, 129.45, 129.40, 128.8, 128.3, 126.2, 56.5, 41.1. HRMS (FAB) *m*/*z* calcd for $C_{39}H_{32}$: 500.2504, found: 500.2504. IR (cm^{-1}): 3024, 1597, 1508, 1492, 1447.

Bis(4-*bis*(4-*fluorophenyl*)*methylphenyl*)*methane* (**6b**). Preparation of the first generation dendritic diarylcarbenium ion pool **5b**

from **3b** (1.93 g, 3.0 mmol) and its reaction with triethylsilane (0.94 mL, 6.0 mmol) afforded a mixture of **6b** (866 mg, 1.51 mmol) as a white solid in 50% yield (isolated yield by preparative GPC). Mp 142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) 7.12 (d, J=8.2 Hz, 4H), 7.06–7.03 (m, 8H), 7.00–6.96 (m, 12H), 5.47 (s, 2H), 3.94 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) 161.4 (d, J=243.5 Hz), 141.3, 139.5 (d, J=3.6 Hz), 139.2, 130.7 (d, J=7.9 Hz), 129.3, 129.0, 115.1 (d, J=21.5 Hz), 54.9, 41.0. HRMS (EI) m/z calcd for $C_{39}H_{28}F_4$: 572.2127, found: 572.2127. IR (cm^{-1}): 2986, 1601, 1504, 1219, 1157.

4.3.3. NMR analysis of the 'cation pool' synthesized from the precursor without trimethylsilyl group. The anodic oxidation was carried out in an H-type divided cell (4 G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca. 100 mg, dried at 250 °C/1 mmHg for 2.5 h before use) and a platinum plate cathode (10 mm×10 mm). In the anodic chamber were placed **6a** (100 mg, 0.200 mmol) and 0.3 M Bu_4NBF_4 in CD_2Cl_2 (5.0 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (35 μL, 0.40 mmol) and 0.3 M Bu_4NBF_4 in CD_2Cl_2 (5.0 mL). The constant current electrolysis (5.0 mA) was carried out at −78 °C with magnetic stirring. After 2.5 F/mol of electricity was consumed, the reaction mixture of the anodic chamber was transferred to a 5 mm ϕ NMR tube with a septum cap under Ar atmosphere at −78 °C. The NMR measurement was carried out at −80 °C. Chemical shifts are reported using the signal of CH_2Cl_2 at δ 5.32 for ^{1}H NMR and δ 53.8 for ^{13}C NMR, respectively. Peaks of δ 9.87 (s, 1H, H^a (integral: 7.16)) and δ 193.9 are selected for determining the existence of diarylcarbenium ion **5a** and peak of δ 4.22 (s, 2H, H^b (integral: 5.52)) and δ 207.0 are selected for determining the existence of triarylcarbenium ion **7**. The conversion of the starting material **6a** (H^c (integral: 9.15)) and the ratio **5a**/**7** are determined from the integral of protons H^a, H^b, and H^c.

4.3.4. The time-course NMR analysis of the first generation of dendritic diarylcarbenium ions. A solution of the first generation of dendritic diarylcarbenium ion **5** (ca. 0.5 mL, ca. 0.02 mmol) in the anodic chamber was transferred to a 5 mm NMR tube with a septum cap under an argon atmosphere at −78 °C. The NMR tube was put into the cooling bath at the second temperature (0 °C or −20 °C). The time-course NMR measurement was performed at the second temperature until the peak of proton H^a disappeared. The decompose profiles in Fig. 6 were obtained from these results (see Supplementary data for details).

4.4. Preparation of the second, the third, and the fourth generation of dendritic organosilicon compounds

The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca. 160 mg, dried at 250 °C/1 mmHg for 2.5 h before use) and a platinum plate cathode (20 mm×10 mm). In the anodic chamber were placed a solution of **3a** (234.8 mg, 0.410 mmol) and 0.3 M Bu_4NBF_4/CH_2Cl_2 (8.0 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (70 μL, 0.79 mmol) and 0.3 M Bu_4NBF_4/CH_2Cl_2 (8.0 mL). The constant current electrolysis (9.0 mA) was carried out at −78 °C with magnetic stirring until 2.7 F/mol of electricity was consumed. Then benzhydryltrimethylsilane (38.3 mg, 0.159 mmol) was added to the anodic chamber at −78 °C and the mixture was stirred for 1 h. The resulting mixture was treated with triethylamine (0.2 mL) at −78 °C. After stirring at room temperature for 10 min, the solvent was removed under reduced pressure and the residue was quickly filtered through a short column (2×3 cm) of silica gel to remove Bu_4NBF_4 by using hexane/AcOEt 1:1 as eluent. Removal of the solvent of the combined filtrate under reduced pressure and the crude product thus-obtained was purified with preparative GPC to obtain **8a** (158 mg, 0.127 mmol) as a white solid in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.28 (m, 16H), 7.24–7.21 (m, 8H), 7.16–7.14 (m, 20H), 7.03–6.99 (m, 20H), 5.53(s, 4H), 5.44 (s, 2H), 3.45 (s, 1H), 0.02 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 142.1, 141.6, 140.7, 140.4, 129.4, 129.3, 129.21, 129.17, 128.4, 128.2, 126.2, 56.5, 55.6, 45.2, −1.7. HRMS (FAB) m/z calcd for $C_{94}H_{80}NaSi$ $[M+Na]^+$: 1259.5922, found: 1259.5927. IR (cm^{-1}): 3024, 1597, 1493, 1450, 1250, 1018.

The second generation dendritic organosilicon compound **8b**. Synthesis of the 'cation pool' from **3b** (1.04 g, 1.61 mmol) and its reaction with benzhydryltrimethylsilane (154 mg, 0.638 mmol) afforded a mixture of **8b** (683 mg, 0.494 mmol) as a white solid in 77% yield (isolated yield by preparative GPC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, J=8.3 Hz, 4H), 7.06–6.96 (m, 52H), 5.46 (s, 4H), 5.41 (s, 2H), 3.43 (s, 1H), −0.01 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.6 (d, J=242.7 Hz), 142.5, 141.4, 140.9, 140.4, 139.6, 130.8 (d, J=7.2 Hz), 129.5, 129.3, 129.1, 128.6, 115.3 (d, J=21.5 Hz), 55.6, 55.0, 45.4, −1.6. HRMS (FAB) m/z calcd for $C_{94}H_{71}F_8Si$ $[M-H]^+$: 1379.5197, found 1379.5184. IR (cm^{-1}): 3036, 1601, 1504, 1223, 1157, 1018.

The third generation dendritic organosilicon compound **10**. Synthesis of the 'cation pool' from **8b** (346 mg, 0.25 mmol) and its reaction with benzhydryltrimethylsilane (24.3 mg, 0.10 mmol) afforded a mixture of **10** (178 mg, 0.062 mmol) as a pale yellow solid in 62% yield (isolated yield by preparative GPC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11–6.92 (m, 121H), 5.45 (s, 8H), 5.42 (s, 4H), 5.38 (s, 2H), 3.42 (s, 1H), −0.01 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.4 (d, J=244.2 Hz), 142.2, 141.5, 141.4, 140.7, 140.4, 139.5, 130.7 (d, J=8.6 Hz), 129.4, 129.3, 129.22, 129.16, 129.06, 128.4, 115.2 (d, J=20.1 Hz), 55.8, 55.7, 54.9, 45.4, −1.7. HRMS (FAB) m/z calcd for $C_{198}H_{144}F_{16}Si$: 2853.0782, found 2853.0764. IR (cm^{-1}): 1601, 1504, 1223, 1157, 1018.

The fourth generation dendritic organosilicon compound **12**. Synthesis of the 'cation pool' from **10** (529.4 mg, 0.185 mmol) and its reaction with benzhydryltrimethylsilane (16.8 mg, 0.070 mmol) afforded a mixture **12** (186 mg, 0.032 mmol) as a pale yellow solid in 46% yield (isolated yield by preparative GPC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, J=8.0 Hz, 8H), 7.00–6.88 (m, 240H), 5.41(s, 16H), 5.38 (s, 8H), 5.35 (m, 6H), 3.41 (s, 1H), −0.03 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (d, J=244.2 Hz), 142.1, 141.9, 141.64, 141.56, 141.4, 140.7, 140.4, 139.4, 130.7 (d, J=7.2 Hz), 129.4, 129.3, 129.2, 129.1, 128.4, 115.1 (d, J=21.5 Hz), 55.8, 55.7, 54.9, 45.3, −1.7. HRMS (FAB) m/z calcd for $C_{406}H_{288}F_{32}AgSi^+$: 5905.0840, found: 5905.0845. IR (cm^{-1}): 1601, 1504, 1223, 1157, 1018.

4.5. The low-temperature and the time-course NMR analyses of the second and the third generation of dendritic diarylcarbenium ions

4.5.1. NMR analysis of dendritic diarylcarbenium ions. The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca. 100 mg, dried at 250 °C/1 mmHg for 2.5 h before use) and a platinum plate cathode (10 mm×10 mm). In the anodic chamber were placed **8a** (166 mg, 0.13 mmol) and 0.3 M Bu_4NBF_4 in CD_2Cl_2 (5.0 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (35 μL, 0.40 mmol) and 0.3 M Bu_4NBF_4 in CD_2Cl_2 (5.0 mL). The constant current electrolysis (5.0 mA) was carried out at −78 °C with magnetic stirring. After 2.5 F/mol of electricity was consumed, the reaction mixture of the anodic chamber was transferred to a 5 mm ϕ NMR tube with a septum cap under Ar atmosphere at −78 °C. The NMR measurement was carried out at −80 °C. Chemical shifts are reported using the methylene signal of CH_2Cl_2 at δ 5.32 (^{1}H NMR) and δ 53.8 (^{13}C NMR) as internal standards, respectively. Selected peaks for **9a**, ^{1}H NMR (600 MHz,

CD_2Cl_2) δ 9.87 (s, 1H), 8.36 (br s, 2H), 8.15 (br s, 2H), 5.70 (s, 2H), 5.52 (s, 4H). ^{13}C NMR (150 MHz, CD_2Cl_2) δ 193.7 (cationic carbon).

The second generation dendritic diarylcarbenium ion **9b**. The NMR measurement was carried out at −80 °C. Selected peaks for **9b**, ^1H NMR (600 MHz, CD_2Cl_2) δ 9.87 (s, 1H), 8.37 (d, J=7.6 Hz, 2H), 8.31 (d, J=6.2 Hz, 2H), 7.63 (d, J=8.2 Hz, 2H), 7.51 (d, J=6.9 Hz, 2H), 7.00–6.88 (m), 5.72 (s, 2H), 5.50 (s, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.7, 167.0, 160.7 (d, J=242.0 Hz), 147.4, 142.3, 139.8, 138.9, 138.3, 135.1, 133.3, 132.3, 130.4 (d, J=6.0 Hz), 129.2, 129.1, 114.7 (d, J=20.2 Hz), 57.5.

The third generation dendritic diarylcarbenium ion **11**. The NMR measurement was carried out at −60 °C. Selected peaks for **11**, ^1H NMR (600 MHz, CD_2Cl_2) δ 9.84 (br s, 1H), 8.31 (br s, 2H), 5.63 (br s, 2H), 5.42 (br s, 12H). Cationic carbon was not observed by ^{13}C NMR.

4.5.2. The time-course NMR analysis of dendritic diarylcarbenium ions. A solution of the second and the third generation of dendritic diarylcarbenium ions (ca. 0.5 mL, ca. 0.01 mmol for **9a**, ca. 0.02 mmol for **9b**, and ca. 0.01 mmol for **11**) in the anodic chamber was transferred to a 5 mm NMR tube with a septum cap under an argon atmosphere at −78 °C. The NMR tube was put into the cooling bath at the second temperature (0 °C or −20 °C). The time-course NMR measurement was performed at the second temperature until the peak of proton H^a disappeared. The decompose profiles in Figs. 7 and 8 were obtained from these results (see Supplementary data for details).

Acknowledgements

This work was partially supported by the Grant-in-Aid for Scientific Research on Innovative Areas (No. 2105) from the MEXT. T.N. thanks the Asahi Glass Foundation and the Research for Promoting Technological Seeds from JST for financial supports. The authors thank Mr. Haruo Fujita, Mr. Tadashi Yamaoka, and Dr. Keiko Kuwata of Kyoto University for assistance in NMR, MS, and X-ray crystal analyses.

Supplementary data

These data include ^1H and ^{13}C NMR spectra, the VT-NMR analyses, and the time-course NMR analyses of dendritic diarylcarbenium ions. Supplementary data related to this article can be found online at doi:10.1016/j.tet.2011.04.065.

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