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Dibromocarbene and bromofluorocarbene addition to substituted allylsilanes

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ABSTRACT

The dibromocarbene or bromofluorocarbene addition to substituted allyldisilanes afforded instable *gem*-dibromocyclopropanes or a *gem*-bromofluorocyclopropane, respectively. These *gem*-bromohalogenocyclopropanes undergo a *spontaneous* ring opening at room temperature to give halogenated dienylsilanes or bromo dienes or dibromotetraenes.

1. Introduction

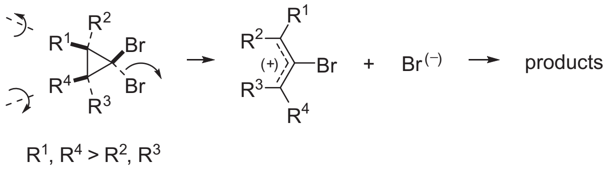
gem-Dibromocyclopropanes are known to give bromoallylic bromides by heating.[1] According to the Woodward–Hoffmann–DePuy rule,[2] a disrotatory electrocyclic ring opening of the cyclopropane with concomitant loss of the bromide anion affords an allylic cation which then captures an anion (Scheme 1). Generally, the ring opening occurs by thermolysis at a temperature >100 °C, but in a few cases, *concerning only strained polycyclic compounds*, the *gem*-dibromocyclopropane is not isolable and the obtained products result from the opening of the cyclopropane followed by the evolution of the bromoallylic cation.

Previously, we have shown that the dibromocarbene addition to the 1,4-bis(trimethylsilyl)but-2-ene **1** and thermolysis of the adduct **2** under vacuum at 100 °C afforded 3-bromo-1-trimethylsilylpenta-2,4-diene **3** in 75% yield (Scheme 2).[3]

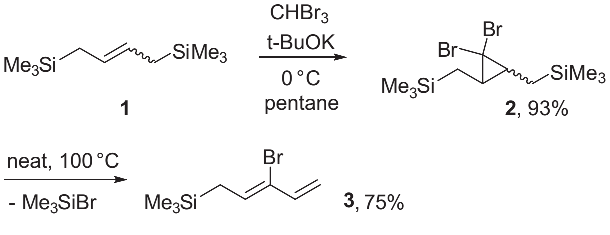
Herein, we report on the dibromocarbene addition[4] to the 2,3-dimethyl-1,4-bis(trimethylsilyl)but-2-ene **4** and the 2,3,6,7-tetramethyl-1,8-bis(trimethylsilyl)octa-2,6-diene **5** resulting from a reductive silylation of the 2,3-dimethylbuta-1,3-diene (Scheme 3).[5]

From **4**, a very clean reaction occurred to give **9** in the good yield of 81% (Scheme 4).[6,7]

The synthesis of product **9** is explained by the instability of adduct **6** and surprisingly a protolysis of **8**. Previously, Magnus obtained **9** by heating 1,1-dibromo-2,2,3,3-tetramethyl-cyclopropane in $PhNMe_2$ at 150 °C.[8] Therefore, in comparison with **1**, the presence of the two additional methyl groups in the disilane **4** induced a spectacular ring opening. To the best of our knowledge,[1] this result corresponds to the first ring opening at room temperature of a monocyclic *gem*-dibromocyclopropane.



Scheme 1. Disrotatory electrocyclic ring opening of *gem*-dibromocyclopropanes.



Scheme 2. Synthesis of the 3-bromo-1-trimethylsilylpenta-2,4-diene **3**.

This result prompted us to synthesise the corresponding fluorine derivative. After addition of bromofluorocarbene to **4**, we have obtained the silylated fluoropentadiene **12** in 72% yield (Scheme 5).[9] There are substantially fewer reports in the literature of bromofluorocarbene.[10] The unprecedented reaction of commercially available ethyl dibromofluoroacetate with sodium

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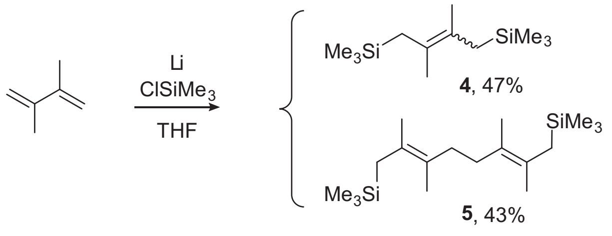
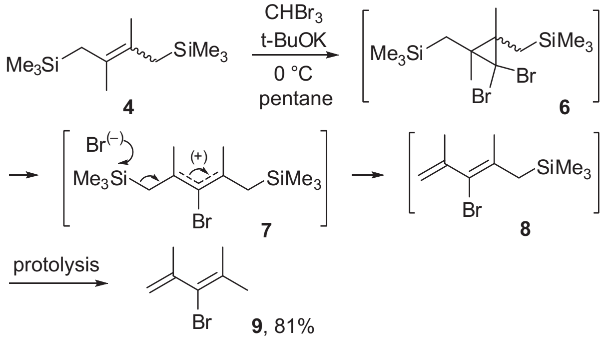
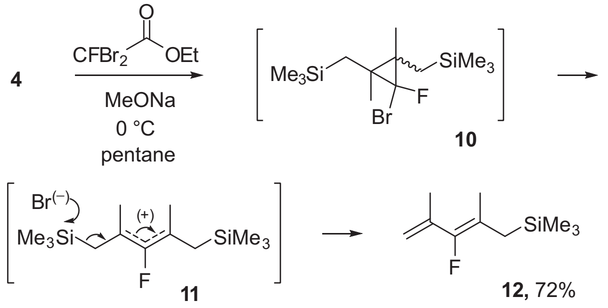


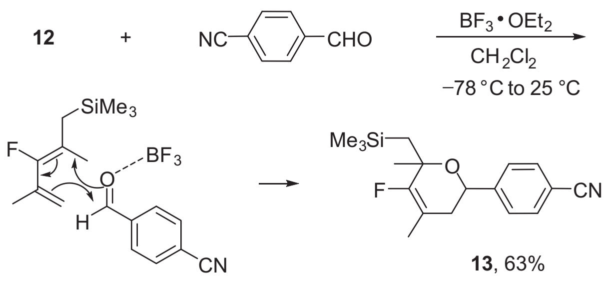
Scheme 3. Reductive silylation of the 2,3-dimethylbuta-1,3-diene.



Scheme 4. Dibromocarbene addition to the 2,3-dimethyl-1,4-bis(trimethylsilyl)-but-2-ene **4**.



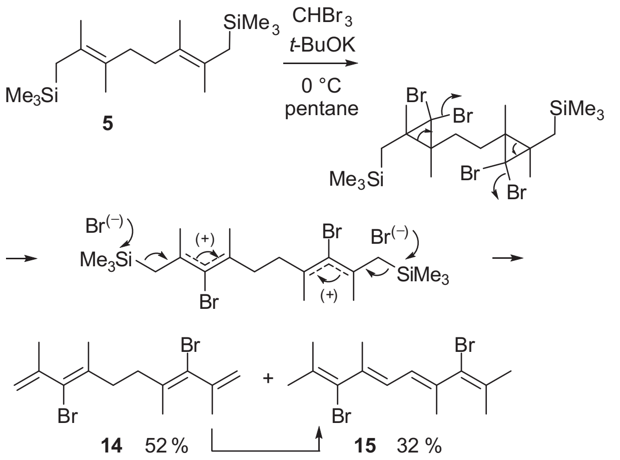
Scheme 5. Preparation of the 3-fluoro-2,4-dimethyl-1-trimethylsilylpenta-2,4-diene **12**.



Scheme 6. Addition of dienylsilane **12** to the *p*-cyanobenzaldehyde.

methylate, carried out in the presence of an alkene, afforded appropriate bromofluorocarbene in good yield.[11] The presence of the fluorine atom did not prevent the spontaneous ring opening of the bromofluorocyclopropane **10** at room temperature. As previously,[3] the more stable transoid configuration of the allylic cation **11** induced the configuration of the double bond of **12**.

Attention was next directed to the Lewis acid promoted addition reaction of **12** to aldehydes. Surprisingly, with the 4-cyanobenzaldehyde, and in the presence of $BF_3{\cdot}Et_2O$, this dienylsilane led to the Diels–Alder adduct **13** (one isomer) in 63% yield (Scheme 6).[12]



Scheme 7. Dibromocarbene addition to the bis(allylsilane) **5**.

In order to extend these results, the bis(allylsilane) **5**[5] was submitted to dibromocarbene addition (Scheme 7). Two dibromides **14** and **15** were obtained and **14** can be isomerized in more stable tetraene **15**.[13] The structure of this latter compound has been confirmed by an X-ray crystallographic analysis, which showed that the molecule is twisted (C_2 axis) with a reduced conjugation (Fig. 1).[14]

The very high stability of the allylic cations **7** and **11** which are bi-tertiary and twice β-silylated[15] explained the easy ring opening of **6** and **10**. Calculations at the B3LYP/6-311++G(3d,3p) level of the theory[16] showed that **7** and **11** are very stable allylic cations compared to the parent cation **16** and the bi-tertiary allylic cation **17** (Fig. 2).

Global electronic indexes, the chemical hardness η,[17] the electronic chemical potential (negative of the electronegativity) μ[18] and the electrophilic power ω,[19] as defined within the density functional theory (DFT) of Parr, Pearson, and Yang,[20] are useful tools to understand the reactivity of molecules in their ground states (Table 1).[21]

$$\eta \approx (E_{\text{LUMO}} - E_{\text{HOMO}})/2;\ \mu \approx (E_{\text{LUMO}} + E_{\text{HOMO}})/2;\ \omega \approx \mu^2/2\eta$$

The global electrophilic power ω measures the stabilization in energy when the system acquires an additional electronic charge ΔN from the environment. A comparison of the electrophilic power values for **7**, ω = 20.1 or **11**, ω = 19.7 and allylic cation **16**, ω = 33.7, shows high values particularly for the allylic cation. Consequently, we can deduce that **7** and **11** (more soft allylic cations) are more stable than the allylic cation **16**.

2. Conclusion

We have shown that from the silylation of 2,3-dimethyl-1,3-butadiene[5] followed by the dibromocarbene or bromofluorocarbene addition, we could obtain valuable halogenated dienes and tetraenes in two steps.

Acknowledgements

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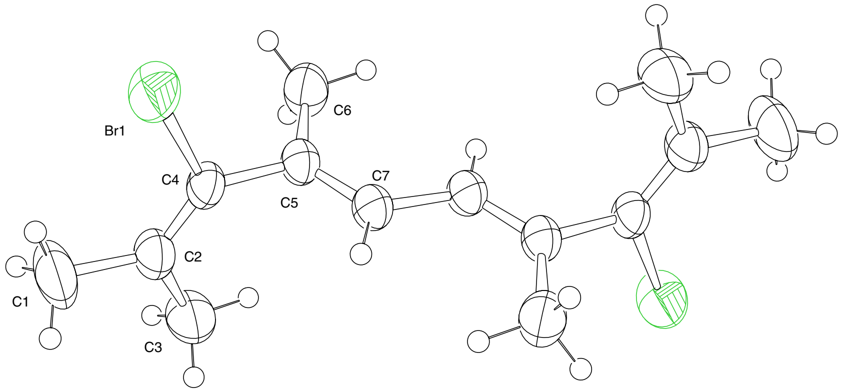
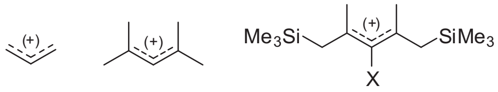


Figure 1. ORTEP drawing of (*E*,*E*)-3,8-dibromo-2,4,7,9-tetramethyldeca-2,4,6,8-tetraene **15**.



16 **17** **7**, X = Br; **11**, X = F

Figure 2. Allylic cations.

Table 1
Computation of global electronic indexes for **7**, **11**, **16** and **17**

Cation	*E* (au)	E_{HOMO} (au)	E_{LUMO} (au)	η (au)	μ (au)	ω (eV)
16	−117.006676	−0.578	−0.387	0.096	−0.483	33.7
17	−274.389914	−0.471	−0.295	0.088	−0.383	22.6
7	−3665.442780	−0.381	−0.247	0.067	−0.314	20.1
11	−1191.181743	−0.388	−0.249	0.070	−0.318	19.7

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6. *General*: All reactions were performed under an argon atmosphere in oven-dried glassware. NMR spectroscopy: Bruker AC 300 (^{1}H = 300 MHz, ^{13}C = 75 MHz); chemical shift δ in parts per million relative to $CDCl_3$ (signals for residual $CHCl_3$ in the $CDCl_3$: 7.26 for ppm for ^{1}H NMR and 77.00 (central) for ^{13}C NMR). Carbon–proton couplings were determined by DEPT sequence experiments. Compounds **4** and **5** were prepared according to the procedure previously reported.[5]
7. 3-Bromo-2,4-dimethylpenta-1,3-diene (**9**).[8] In a 250 mL three-necked flask equipped with a thermometer, a septum cap, a magnetic stirring bar, and an argon outlet was charged with potassium *tert*-butoxide (11.8 g, 105 mmol) in anhydrous pentane (60 mL). The mixture was cooled to 0 °C and **4** (8 g, 35 mmol) was added. Then, bromoform (9.4 mL, 26.6 mmol) was slowly added with a syringe. After 1 h of stirring at 0 °C and 1 h at rt, the mixture was filtered on Celite® and the filtrate was stirred with brine. After usual work-up (Et_2O), the crude product was flash chromatographed (petroleum ether) to give **9** (37.5 g, 21.5 mmol, 81%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.02 (s, 1H), 4.89 (s, 1H), 1.88 (s, 3H), 1.87 (s, 3H), 1.79 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.2 (s), 131.0 (s), 120.3 (s), 116.6 (t), 25.4 (q), 24.6 (q), 21.9 (q).
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9. 3-Fluoro-2,4-dimethyl-5-trimethylsilylpenta-1,3-diene (**12**). To a mixture of sodium methoxide (0.82 g, 15.2 mmol) and **4** (1.5 g, 6.6 mmol) in anhydrous pentane (15 mL) under argon, stirred to 0 °C, was slowly added ethyl dibromofluoroacetate (1.2 mL, 13.2 mmol). After stirring for 8 h at 0 °C and 12 h at rt, the mixture was filtered on Celite® and the filtrate was stirred with brine. After usual work-up (pentane), the crude product was flash chromatographed (petroleum ether) to give **12** (0.88 g, 4.75 mmol, 72%) as an oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.09 (s, 1H), 4.97 (s, 1H), 1.86 (s, 3H), 1.72 (s, 3H), 1.69–1.67 (m, 2H), 0.03 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.8 (d, ${}^2J^{(CF)}$ = 31.6 Hz), 136.8 (d, ${}^2J^{(CF)}$ = 30.2 Hz), 131.4 (q, ${}^1J^{(CF)}$ = 254.7 Hz), 116.7 (t), 21.8 (t), 20.9 (q), 20.1 (q), 0.9 (q); ^{19}F NMR ($CDCl_3$, 282.4 MHz) δ −112.9 (s). HRMS for $[C_{10}H_{19}FSi]^+$, 186.1240; found: 186.1235.
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12. 6-(4-Cyanophenyl)-3-fluoro-2,4-dimethyl-2-trimethylsilyl-methyl-5,6-dihydro-2*H*-pyran (**13**). To 4-cyanobenzaldehyde (0.04 g, 0.32 mmol) in anhydrous CH_2Cl_2 (5 mL) under argon, stirred to −78 °C, were slowly added $BF_3{\cdot}Et_2O$ (0.05 mL, 0.4 mmol) and then **12** (0.12 g, 0.64 mmol). After stirring for 1 h at −78 °C and 18 h at rt, the mixture was filtered on Celite® and the filtrate was stirred with brine. After usual work-up (CH_2Cl_2), the crude product was flash chromatographed (petroleum ether/ether, 80:20) to give **13** (0.064 g, 0.20 mmol, 63%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.63 (d, *J* = 6.0 Hz, 2H), 7.49 (d, *J* = 6.0 Hz, 2H), 4.80 (dd, *J* = 3.0, 9.0 Hz, 1H), 2.16 (s, 3H), 1.66 (s, 2H), 1.40 (s, 3H), 0.90 (dd, 3.0, 9.0 Hz, 2H), 0.05 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.5 (s), 147.5 (s), 132.4 (d) (2C), 126.0 (d) (2C), 119.0 (s), 111.3 (s), 105.7 (q, ${}^1J^{(CF)}$ = 285.0 Hz), 73.4 (s), 70.0 (d), 38.1 (t), 29.8 (t), 26.7 (q), 13.8 (q), 1.1 (q). Elemental Anal. Calcd for $C_{18}H_{24}FNOSi$ (317.47): C, 68.10; H, 7.62. Found: C, 68.19; H, 7.71.
13. 3,8-Dibromo-2,4,7,9-tetramethyldeca-1,3,7,9-tetraene (**14**) and (*E*,*E*)-3,8-dibromo-2,4,7,9-tetramethyldeca-2,4,6,8-tetraene (**15**). Following the procedure described for **9**, to *t*-BuOK (3.3 g, 29.1 mmol) in pentane (40 mL) and disilane **5** (4.34 g, 14 mmol) was slowly added bromoform (2.6 mL, 29.1 mmol). After stirring for 1 h at 0 °C and 2 h at rt, usual work-up and flash chromatography on silica gel (petroleum ether), gave **14** (2.52 g, 7.3 mmol, 52%) as an oil and **15** (1.55 g, 4.5 mmol, 32%) as white crystals. Compound **14**, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.92 (s, 2H), 4.88 (s, 2H), 2.28 (t, *J* = 3.8 Hz, 4H), 1.88 (s, 6H), 1.85 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.2 (s), 144.0 (s), 133.9 (s), 116.6 (t), 35.4 (t), 21.3 (q), 20.1 (q). **15**, mp 92 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.15 (s, 2H), 1.91 (s, 6H), 1.87 (s, 6H), 1.79 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.8 (s), 131.3 (s), 126.2 (d), 122.8 (s), 24.8 (q), 22.2 (q), 16.5 (q).
14. X-ray Crystallography: CCDC-794285 (for **15**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk].
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