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Chemistry

Electrochemical preparation of tris(*tert*-butyldimethylsilyl)cyclopropene and its hydride abstraction to tris(*tert*-butyldimethylsilyl)cyclopropenium tetrafluoroborate

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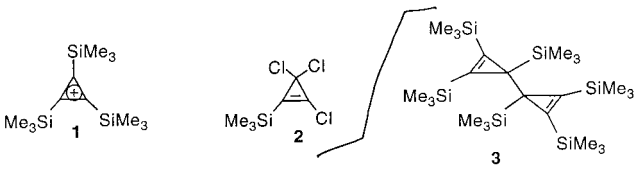
ABSTRACT **Electrochemical reductive *tert*-butyldimethylsilylation of tetrachlorocyclopropene to 1,2,3-tris(*tert*-butyldimethylsilyl)cyclopropene, a potential strained precursor for Diels–Alder and related cycloaddition reactions, is described. By hydride abstraction with nitrosonium tetrafluoroborate, 1,2,3-tris(*tert*-butyldimethylsilyl)cyclopropene is ionized quantitatively to Hückeloid 2π aromatic tris(*tert*-butyldimethylsilyl)cyclopropenium tetrafluoroborate.**

Cyclopropenes and cyclopropenium ions are versatile building blocks for organic synthesis (1–3). Because of a combination of steric bulkiness and σ-donor ability, silylated cyclopropenes and cyclopropenium ions in particular (similar to **1**), are expected to be of great synthetic importance for the preparation of highly strained compounds via cycloaddition and related reactions (1, 2, 4). Furthermore, inclusion of silyl groups provides the possibility to use them as functionality for conversion (electrophilic substitution) on a later step of syntheses (5). However, the preparation of silylated cyclopropenes has generally remained a difficult task involving multistep synthesis (4). Garratt and Tsotinis have prepared tris(trimethylsilyl)cyclopropene by reacting chloromethyltrimethylsilane with bis(trimethylsilyl) acetylene in the presence of a strong base in 15% yield (6). de Meijere *et al.* have also managed to obtain the crystal structure of **1** with the hexachloroantimonate anion (7).†

In the course of our studies of the electrophilic substitution of aromatic cations, we were interested in the development of convenient procedures for the preparation of silylated cyclopropenes (8, 9). The attempt to silylate tetrachlorocyclopropene **4** with chlorotrimethylsilane under Barbier conditions resulted in the coupling of the cyclopropene moieties to hexakis(trimethylsilyl)-3,3′-bicyclopropenyl **3** in preparatively useful yield (10). Use of *tert*-butyldimethylchlorosilane under these conditions did not give the coupling but led to tetrakis(*tert*-butyldimethylsilyl)cyclopropene in 1.8% yield, leaving no functionality for conversion into the corresponding cyclopropenium ion (11). Recently, we reported the selective monotrimethylsilylation of tetrachlorocyclopropene **4** to 1-trimethylsilyltrichlorocyclopropene **2** (8). However, further stepwise trimethylsilylation of **4** did not give the tris(trimethylsilyl)cyclopropene, but resulted in formation of hexakis(trimethylsilyl)-3,3′-bicyclopropenyl **3** (9). We report now the electrochemical one-step synthesis of 1,2,3-tris(*tert*-butyldimethylsilyl)cyclopropene **5** from readily available tetrachlorocyclopropene **4** (commercially available from Aldrich, Kodak, and Merck) and its subsequent ionization to the cyclopropenium salt tris(*tert*-butyldimethylsilylcyclopropenium tetrafluoroborate **6**.



Reaction of **4** in a 10:1 mixture of tetrahydrofuran and hexamethylphosphoramide in a single compartment (ref. 13; cell volume 120 ml, aluminum rod anode, stainless steel net cathode) electrochemical cell with *tert*-butyldimethylchlorosilane and six Faraday current per mol gave 1,2,3-tris(*tert*-butyldimethylsilyl)cyclopropene **5** after workup in 12–15% isolated yield. Attempts to further improve the reaction failed. However, taking into consideration the ready availability of the starting compounds and the single-step multifold functionalization of the cyclopropene, the low yield of the reaction is acceptable, particularly when considering its nearly quantitative subsequent ionization to cyclopropenium ion (see below). The reactions were typically carried out on a 2- to 3-g scale under a constant current of 50 mA with tetra-*n*-butylammonium bromide as the electrolyte support with an aluminum rod anode and a stainless steel net cathode. Essential for minimizing oligomeric side products was the initial slow addition (during the first two Faraday of current) of the tetrachlorocyclopropene to the reaction mixture. This was achieved by adding **4** in tetrahydrofuran solution to the cell via syringe pump over a period of 15 hr. In addition, a low current density of $j = 5$ A/m^2 provided a low concentration of **4** and allowed facile product analysis at the cathode (typical procedure for electrochemical synthesis of **2**). The reaction was monitored by GC/MS, which indicated that the silylation in the first two reduction steps took place on the olefinic positions, in agreement with the earlier observations for the electrochemical trimethylsilylation of **4** (9). As indicated by a crossover in the cyclic voltammogram of **4** (8), further reduction of the allylic carbon chlorine bonds in **4** takes place by electron transfer/disproportionation resulting in silylation and hydrogen transfer to this position from the solvent or the electrolyte. In contrast to the reaction with chlorotrimethylsilane, only a trace of the coupling to product bicyclopropenyl was observed by GC/MS in the reaction mixture (ref. 9; the coupling product appears to be 1,2, 1′, 2′-tetrakis (*tert*-butyldimethyl-silyl)-3,3′-bicyclopropenyl). As indicated by the ^{13}C NMR at 23°C of **5,** there is hindered rotation around the silicon carbon bonds on the olefinc positions. The ^{13}C NMR spectrum shows two different signals at -4.8 and -4.7 ppm for the methyl groups attached to the vinylic silicons. The silicon-attached methyl

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†This is Part 202 in the series "Synthetic Methods and Reactions" and was presented in part as Paper No. 471 at the 207th American Chemical Society National Meeting, March 13–17, 1994 (San Diego, CA).

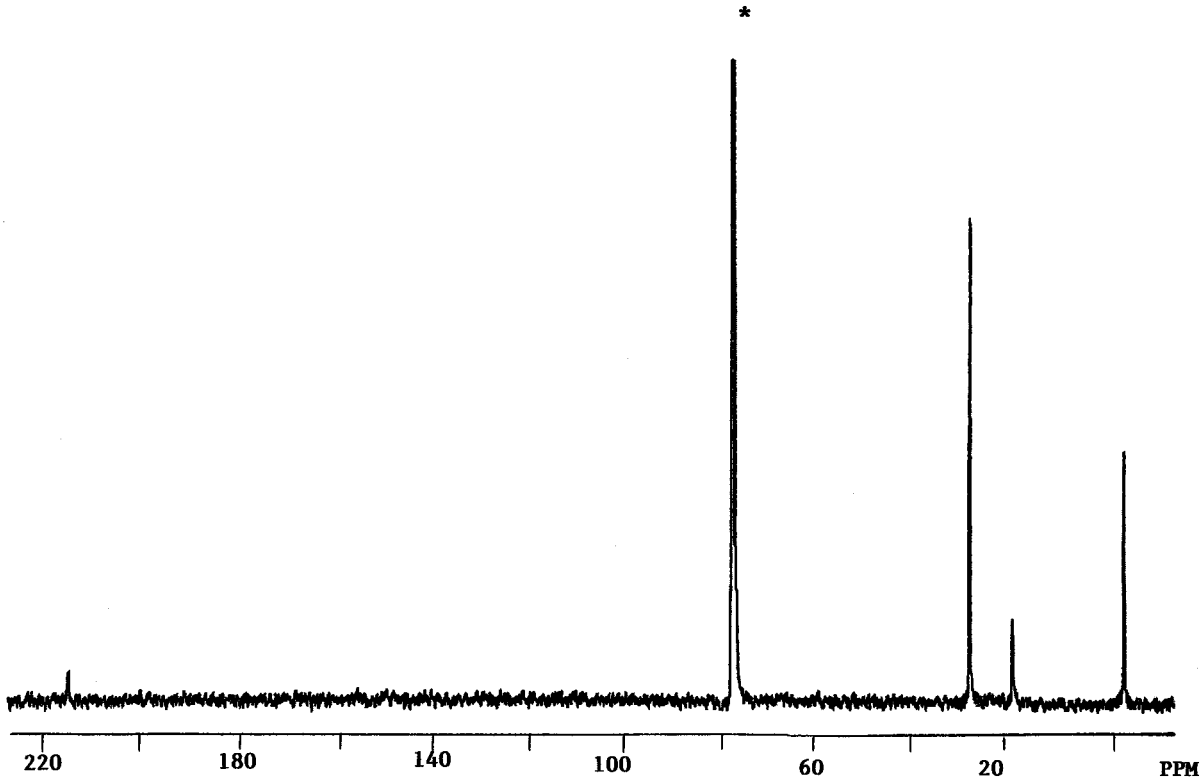
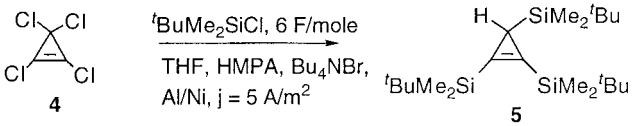
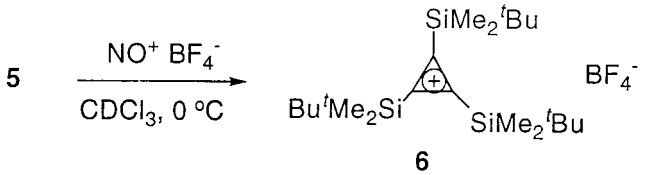


FIG. 1. Proton-decoupled (75 MHz) ^{13}C NMR spectrum of tris (*tert*-butyldimethylsilyl)cyclopropenium tetrafluoroborate (**6**) in $CDCl_3$ solution at ambient temperature. *, caused by $CDCl_3$.

groups for the allylic *tert*-butyldimethylsilyl group were observed at −6.00 ppm.‡



All attempts of hydride abstraction of **5** by triphenylmethyl tetrafluoroborate to the corresponding 2π aromatic cyclopropenium ion failed because of the steric bulk of both reactants. Even after heating under reflux in chloroform, no reaction ensued as detected by NMR. However, almost instant reaction to tris(*tert*-butyldimethylsilyl)cyclopropenium tetrafluoroborate **6** was achieved by treating a solution of **5** in chloroform with nitrosonium tetrafluoroborate at 0°C. After precipitation with pentane, **6** was obtained analytically pure in almost quantitative yield.§



The effect of silyl substituents on the reactivity and stability of carbocationic reactive intermediates has been extensively studied by ^{13}C NMR spectroscopy (13). Particularly interesting is the effect of α- and β-silicon groups on unsaturated organic moieties. The ^{13}C NMR of **6** (Fig. 1) in deuterochloroform shows four signals. The signal for the three ring carbons of the 2π aromatic cyclopropenium moiety was observed at δ ^{13}C 217.1, showing clearly the highly deshielding influence of silicon on the sp^2 hybridized cationic ring carbons. Comparison of this value with tris(trimethylsilyl)cyclopropenium hexachloroantimonate (214.3 ppm) shows only a small influence of the substitution pattern on silicon on the ring carbons (4).

In conclusion, we have developed a convenient two-step preparation of tris(*tert*-butyldimethylsilyl)cyclopropenium tetrafluoroborate **6** from readily available starting materials. Its convenient properties (including stability and solubility) and ease of preparation make it a promising synthon. Exploration of synthetic applications of **6** is under way.

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‡The compound **5** was obtained as a thick oily liquid (0.9 g, 15% yield, from ≈3 g of tetrachlorocyclopropene) after chromatographic separation on neutral alumina (petroleum ether elution) mass spectrum: m/e 382 (M^+), 367, 325, 267, 227, 211, 195, 73. ^1H NMR (300 MHz, $CDCl_3$) δ^1H −0.243 (s, 6H, CH_3), 0.146 (s, 6H, CH_3), 0.151 (s, 6H, CH_3), 0.890 (s, 18H, ^{t}Bu-CH_3), 0.924 (s, 9H, ^{t}Bu-CH_3), 1.255 (s, 1H, C-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ ^{13}C = −6.0 (q), −4.8 (q), −4.7 (q), 4.5 (d), 17.3 (s), 17.7 (s), 27.0 (q), 27.2 (q), 132.7 (s).

§To a solution of **5** (77 mg, 0.2 mmol) in water-free chloroform in an argon atmosphere, 1.1 molar equivalent of nitrosonium tetrafluoroborate (26 mg) was added in small portions at 0°C until no gas evolution was detected. Solids were filtered off, and pentane was added to aid precipitation of **6**. The ionic salt **6** was obtained as a slightly hygroscopic white crystalline solid, mp (uncorrected) 152°C (decomposed), ^1H NMR (300 MHz, $CDCl_3$) δ = 0.579 (s, 18H, CH_3), 0.983 (s, 27H, ^{t}Bu-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta^{13}C$ = −6.00 (q), 17.4 (s), 26.2 (q), 217.2 (s). In comparison, the ^{13}C NMR chemical shift of trichlorocyclopropenium terachloroaluminate is $\delta^{13}C$ 131.

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