

Electrochemical Synthesis of Hexakis(trimethylsilyl)-3,3'-bicyclopropenyl¹

G. K. Surya Prakash,* Herwig A. Buchholz,
Denis Deffieux, and George A. Olah*

Loker Hydrocarbon Research Institute and Department of
Chemistry, University of Southern California,
Los Angeles, California 90089-1661

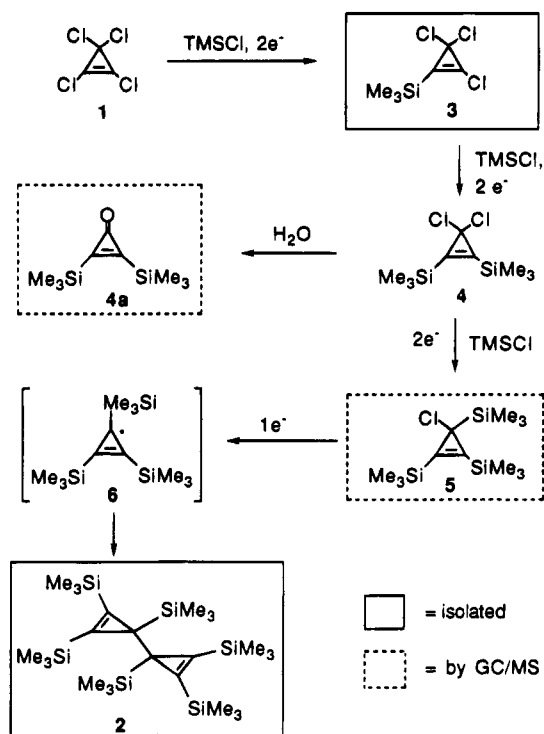
Received July 11, 1994

The synthesis of valence isomers of benzene has attracted the interest of chemist for more than a century.² Only recently the synthesis of the last missing isomer, 3,3'-bicyclopropenyl, has been accomplished³ and its structure crystallographically⁴ determined. Above 10 °C it slowly decomposes and unlike the other valence isomers does not revert to benzene.³ However, due to a "Korsetteffekt"⁵ with bulky groups, substituted bicyclopropenyls like hexa-*tert*-butyl-3,3'-bicyclopropenyl⁶ or hexaphenyl-3,3'-bicyclopropenyl⁷ are stable under these conditions. They are of considerable interest for the studies of the reactions and "through bond" interactions⁸ of the two isolated double bonds in these systems.

We described recently⁹ the synthesis of hexakis(trimethylsilyl)-3,3'-bicyclopropenyl (**2**) in a one-step Barbier-type reaction of tetrachlorocyclopropene with chlorotrimethylsilane. Due to the special effects of the trimethylsilyl groups,¹⁰ **2** is extraordinarily stable and its chemistry different¹¹ from its *tert*-butyl⁶ and phenyl⁷ derivatives. In the course of our studies to explore electrophilic substitution of aromatic cations we were interested in the development of convenient procedures for the preparation of silylated cyclopropenes.¹² We report now the selective electrochemical synthesis of hexakis(trimethylsilyl)-3,3'-bicyclopropenyl **2** from readily available tetrachlorocyclopropene (**1**) and some mechanistic studies on its electrochemical formation.

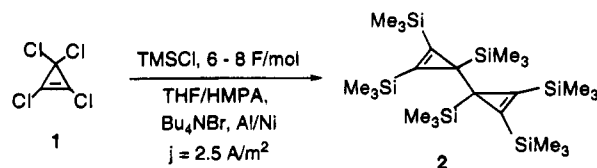
The reaction of **1** with chlorotrimethylsilane in a 10:1 mixture of THF and HMPA by applying 8 Faraday current per mol gave hexakis(trimethylsilyl)-3,3'-bicyclopropenyl after workup in 40% isolated yield. The

Scheme 1. Proposed Mechanism for the Electrochemical Formation of **2** from Tetrachlorocyclopropene with Chlorotrimethylsilane



reactions were carried out on a 2 g scale under constant current in a single compartment electrochemical cell¹³ equipped with an aluminum rod anode and a stainless steel net cathode and tetra-*n*-butylammonium bromide as electrolyte. We have also investigated the influence of the anode material on the reaction. The best results were obtained with an aluminum rod anode. Zinc gave the same reaction; however, the yields were somewhat lower and the workup was difficult due to the formation of zinc hydroxide. No or very little product was detected using a magnesium rod anode.

All attempts to obtain a crystal structure of **2** failed due to the highly disordered packing of **2** in the crystals.¹⁴



The cyclic voltammogram¹² of tetrachlorocyclopropene (**1**) shows clearly two two-electron reduction steps at -1.15 and -2.20 V vs Ag/Ag⁺. Increasing of the potential led to a crossover. The overall reaction is irreversible. By monitoring the reaction by GC/MS the first detectable product after applying 2 Faraday per mol of **1** to the reaction mixture was 1-(trimethylsilyl)trichlorocyclopropene **3** (Scheme 1). **3** has also been isolated.¹² NMR spectroscopic analysis showed clearly the substitution of a vinyl chlorine due to the more favorable formation of a

(13) Heintz, M.; Sock, O.; Saboureaux, C.; Troupel, M. *Tetrahedron* **1988**, *44*, 1631. Cell volume 120 mL, aluminum rod anode, stainless steel net cathode.

(14) We thank Prof. Roland Boese, Universität-Gesamthochschule Essen, for his attempts to obtain the X-ray structure.

(1) (a) Synthetic methods and reaction. 194. For 193 see ref 12. (b) In part presented at the 207th American Chemical Society National Meeting, Paper No. 471, San Diego, CA, March 13-17, 1994.

(2) Potgieter, J. H. *J. Chem. Ed.* **1991**, *68*, 281.

(3) Billups, W. E.; Haley, M. M. *Angew. Chem.* **1989**, *101*, 1735; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1711.

(4) Boese, R.; Blaaser, D.; Gleiter, R.; Pfeifer, K. H.; Billups, W. E.; Haley, M. M. *J. Am. Chem. Soc.* **1993**, *115*, 743.

(5) Maier, G. *Angew. Chem.* **1988**, *100*, 317; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 309.

(6) Maier, G.; Schick, A.; Bauer, I.; Boese, R.; Nussbaumer, M. *Chem. Ber.* **1992**, *125*, 2111.

(7) Breslow, R.; Gal, P. *J. Am. Chem. Soc.* **1959**, *81*, 4747. Breslow, R.; Gal, P.; Chang, H. W.; Altman, L. J. *J. Am. Chem. Soc.* **1965**, *87*, 5139.

(8) Spanget-Larsen, J.; de Korschagen, C.; Eckert-Maksic, M.; Gleiter, R. *Helv. Chim. Acta* **1982**, *65*, 968. Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978. Padon-Row, M. N.; Jordan, K. D. In *Modern Models of Bonding and Delocalization*; Liebman, J. F.; Greenberg, A., Eds.; Verlag Chemie: Weinheim, 1988.

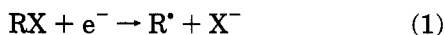
(9) Prakash, G. K. S.; Quaiser, S.; Buchholz, H. A.; Casanova, J.; Olah, G. A. *Synlett* **1994**, *2*, 113.

(10) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1965**, *107*, 3811. Maier, G.; Born, D.; *Angew. Chem.* **1989**, *101*, 1085; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1050. Maier, G.; Volz, D.; Neudert, J. *Synthesis* **1992**, 561.

(11) Sakamoto, K.; Saeki, T.; Sakurai, H. *Chem. Lett.* **1993**, *11*, 1675.

(12) Prakash, G. K. S.; Buchholz, H. A.; Deffieux, D.; Olah, G. A. *Synlett*, in press.

vinyl anion during the reaction. With further reaction **3** disappeared and after hydrolysis the doubly trimethylsilylated cyclopropenone **4a** was identified by GC/MS, resulting from the 1,2-bis(trimethylsilyl)dichlorocyclopropene **4** in the reaction mixture. This is in accordance with the second reduction step in the cyclic voltammogram of **1**. This trimethylsilylation step again involves a more stabilized vinyl anion. After the second trimethylsilylation the situation becomes more complicated. In the course of the reaction the next detectable product besides small amounts of already formed **2**¹⁵ is the tris(trimethylsilyl)chlorocyclopropene **5**. Generally the mechanism for the electrochemical reduction of alkyl halides involves the two following consecutive reactions:¹⁶



The first step is a one-electron reductive cleavage of the carbon-halogen bond (1). In competition with dimerization the radical can be further reduced to a carbanion by transfer of a second electron (2). In the case of **4** no radical dimerization product was detected. On the other hand formation of an anionic intermediate, which was proposed by Breslow et al., should be an antiaromatic species.¹⁷ By α -elimination this α -chlorocyclopropenyl anion should readily give the corresponding carbene or it could react with chlorotrimethylsilane to **5**. However, no evidence for the formation of a carbene from **4** was

(15) The formation of **2** in this stage is probably due to the fact that **5** is more easily reduced than is **4**.

(16) Cleary, J. A.; Mubarak, M.; Vieira, K. L.; Anderson, M. R.; Peters, D. G. *J. Electroanal. Chem.* **1986**, *198*, 107. Andrieux, C. P.; Gallardo, I.; Saveant, J.-M. *J. Am. Chem. Soc.* **1989**, *111*, 1620.

(17) Breslow, R.; Dowd, P. *J. Am. Chem. Soc.* **1963**, *85*, 2729.

obtained. Breslow et al.¹⁸ and Shono et al.¹⁹ have investigated the electrochemical dimerization of the triphenylcyclopropenyl radical. Our results for the dimerization of radical intermediate **6** to **2** are in agreement with the electrochemical formation of hexaphenyl-3,3'-bicyclopropenyl.

In conclusion we have developed an electrochemical trimethylsilylation of tetrachlorocyclopropene to hexakis(trimethylsilyl)-3,3'-bicyclopropenyl (**2**). Mechanistic investigation of the electrochemical reaction of **1** with chlorotrimethylsilane shows that the first two trimethylsilylations occur at the vinyl positions. After introduction of the third trimethylsilyl group a radical coupling of the tris(trimethylsilyl)cyclopropenyl radical yields **2**.

Experimental Procedure

Electrochemical Synthesis of 2. An amount of 2 g (11.4 mmol) of tetrachlorocyclopropene, 10 mL of chlorotrimethylsilane, 10 mL of HMPA, and 0.5 g of tetra-*n*-butylammonium bromide were dissolved under argon atmosphere in 80 mL of THF in a single compartment electrochemical cell⁸ equipped with an aluminum rod anode and stainless steel net cathode. After an hour of preelectrolysis at 50 mA the current was raised to 100 mA ($j = 2.5 \text{ A/m}^2$) and a total of 8 F current per mol of **1** was applied. The reaction mixture was monitored by GC/MS. After the reaction was complete the solvent and remaining chlorotrimethylsilane were distilled off, 100 mL ether was added and the mixture extracted twice with 100 mL cold water. The remaining organic layer was dried over magnesium sulfate and the solvent and most of the disiloxane were removed. Kugelrohr distillation (180–200 °C, 10^{-2} Torr) and subsequent recrystallization from methanol gave 1.16 g (40%) of **2**: mp 240–241 °C, lit. 241 °C. The material gave identical ¹H, ¹³C, and ²⁹Si NMR data as reported.⁹

Acknowledgment. Support of this work by the Office of Naval Research is gratefully acknowledged.

(18) Breslow, R.; Drury, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 4702.

(19) Shono, T.; Toda, T.; Oda, R. *Tetrahedron Lett.* **1970**, *5*, 369.