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Reactions of Perfluoro-1-chloro-2-trimethylsilylcyclobutene.

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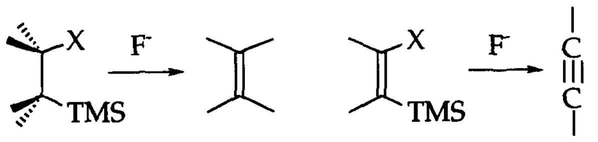
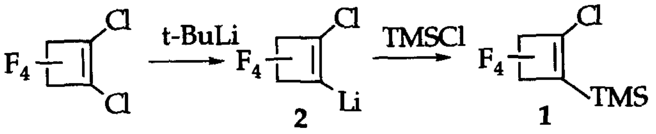
Abstract: The reaction of perfluoro-1,2-dichlorocyclobutene with t-butyllithium leads to replacement of Cl by Li. The lithio derivative was stable to -30°C and reaction with trimethylsilyl chloride gave perfluoro-1-chloro-2-trimethylsilylcyclobutene. The reaction of the latter with t-butyllithium leads to dehalogenation and the addition of t-butyl to form a dimeric compound. The reaction of 1-chloro-2,2,3,3-tetrafluorocyclobutene with phenyllithium followed by treatment with deuterium oxide gave perfluoro-1-phenylcyclobutene-2-d_1, suggesting that perfluorocyclobutyne may have been an intermediate. © 1997 Elsevier Science Ltd. All rights reserved.

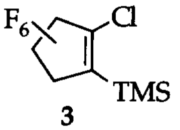
Compounds having halogens and trimethylsilyl groups at adjacent carbons have proven to be useful precursors for forming double or triple bonds via fluoride ion promoted dehalosilylation.[1] Our interest in the possible formation of perfluorocyclobutyne led us to examine the preparation of perfluoro-1-chloro-2-trimethylsilylcyclobutene (**1**). The use of the perfluoro compounds was suggested by indications that fluorines may stabilize some small ring compounds.[2]



The reaction of perfluoro-1,2-dichlorocyclobutene[3] with t-butyllithium in ether led to the replacement of one chlorine by lithium, forming **2**. It was found to be stable up to -30°C and could be observed by NMR spectroscopy. The reaction with trimethylsilyl chloride gave **1**.[4,5] The gas-phase dehalosilylation of **1** has been studied and will be reported separately.[6]



This type of reaction could be used with a variety of related compounds, allowing the preparation of compounds such as **3-5**.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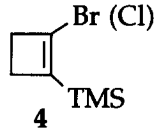
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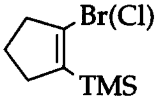
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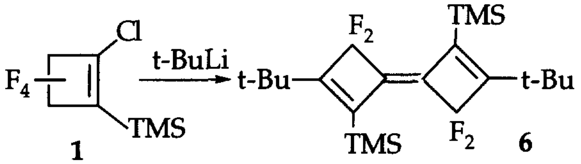
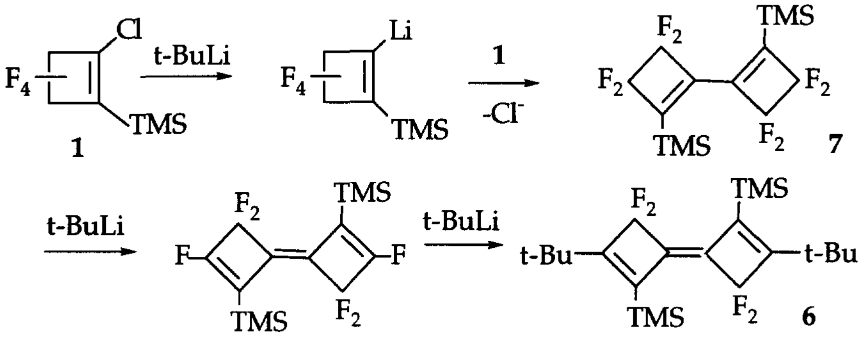
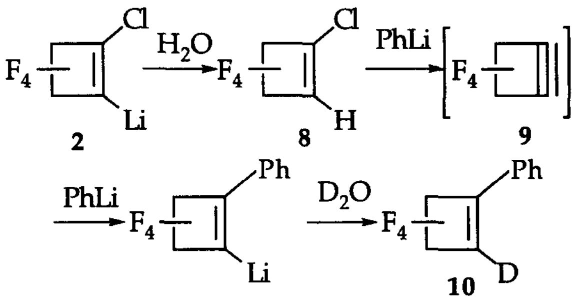
Perfluoro-1,2-bis-(trimethylsilyl)cyclobutene also was of interest in connection with the gas phase synthesis of the perfluorocyclobutyne radical anion using the method of Wenthold, et. al.[7] An attempt was made to prepare this compound via the reaction of **1** with t-butyllithium followed by treatment with trimethylsilyl chloride. This led to a new compound, **6**, in 76% yield, and the same compound was formed if the trimethylsilyl chloride was not added. It had a singlet in the ^{19}F NMR spectrum and had a very simple ^{1}H nmr spectrum. Its structure was determined via X-ray crystallography (Figure 1).



The initial reaction of **1** with t-butyllithium probably occurs at the chlorine, which could be followed by reaction of the anion thus formed with a second molecule of **1** and the loss of chloride ion forming **7**. A possible route to **6** involves further dehalogenation and the addition of t-butyl groups via addition/elimination reactions.



The lithio derivative, **2**, on treatment with water gave the monochloro compound, **8**. The reaction of **8** with phenyllithium led to replacement of the chlorine by phenyl giving **10**. When the reaction mixture was worked up with deuterium oxide, one deuterium was introduced into **10**. The treatment of unlabeled **10** with phenyllithium under the reaction conditions, followed by D_2O, did not introduce deuterium. The introduction of the phenyl group might have occurred via an addition-elimination sequence, but then it is difficult to see how the deuterium is introduced. A simpler hypothesis is that the initial reaction is elimination of HCl giving perfluorocyclobutyne (**9**), followed by addition of phenyllithium. A similar transformation has been observed in the reaction of 1-chlorocyclopentene with phenyllithium.[8]



The availability of compounds such as **3**, **4** and **5** allows the study of ring size and fluorine effects on reactions such as the above, and these reactions are being explored.

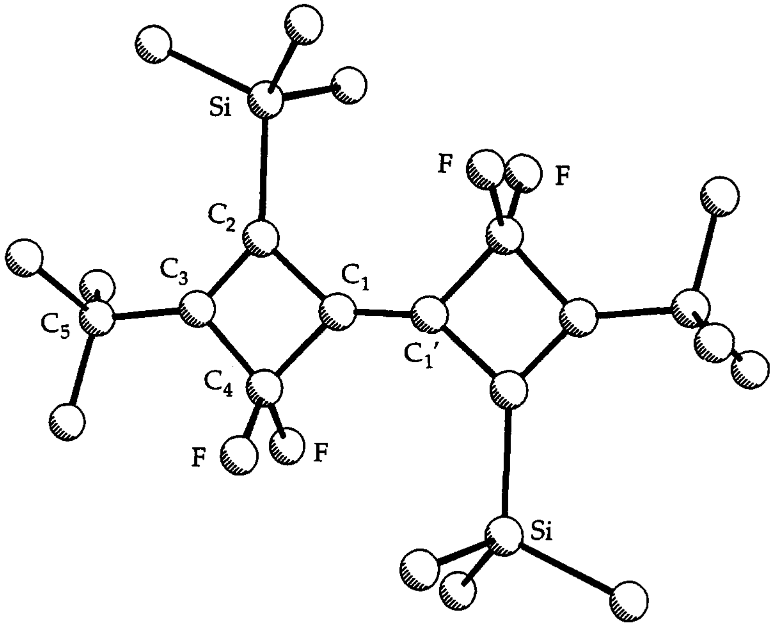


Figure 1. Structure of compound **6** with the hydrogens not shown. The bond lengths are: C_1-C_2 = 1.517(6), C_2-C_3 = 1.368(6), C_3-C_4 = 1.488(7), C_1-C_4 = 1.514 (6), C_1-C_1' = 1.322(6), C_2-Si = 1.901(5), C_3-C_5 = 1.503(7), C_4-F = 1.362(6).

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References and footnotes:

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[2] Rahman, M. M.; Secor, B. A.; Morgan, K. M.; Shafer, P. R.; Lemal, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5986 and references therein. Cf. Johnson, R. P.; Daoust, K. J. *J. Am. Chem. Soc.* **1995**, *117*, 362, ref. 35 for a suggestion that perfluorocyclobutyne may undergo rearrangement less readily than cyclobutyne.

[3] The perfluoro-1,2-dichlorocycloalkenes were purchased from PCR, Inc.

[4] A similar reaction using sodium has been reported by HariPrased, S.; Nagendrappa, G. *Tetrahedron* **1994**, *49*, 3387, but in our hands this reaction was irreproducible. The use of an alkyllithium leads to a clean reaction and a high yield of the product.

[5] All the new compounds were characterized by high resolution mass spectrometry and had the correct exact mass.

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