A 1,2-Silicon Shift in Cyclopropylidenes leading to 1-Trialkylsilylcyclopropenes

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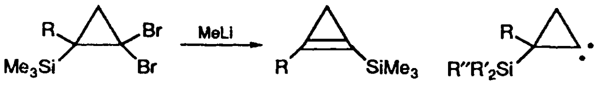
1,1-Dibromo-2-trialkylsilylcyclopropanes, readily prepared by dibromocyclopropanation of vinyltrialkylsilanes, react with methyllithium at −90 to 20 °C to give high yields of trialkylsilylcyclopropenes in which the silicon has apparently migrated to C-1.

The reaction of a 1,1-dibromocyclopropane with methyllithium has been known for many years to lead to a cyclopropylidene or a related 1-bromocyclopropyllithium depending on the temperature and other substituents. In many cases the cyclopropylidene rearranges very efficiently and rapidly to an allene; in other instances, it may be trapped either by addition to carbon–carbon double bonds, insertion into single bonds, ylide-formation with heteroatoms or by rearrangement.[1] The bromocyclopropyllithium may often be trapped by reaction with a range of electrophiles. In contrast, the reaction of a 1,1,2-trihalogeno-2-trialkylsilylcyclopropane with an alkyllithium leads to 1,2-dehalogenation and the formation of a 1-halogeno-2-trialkylsilylcyclopropene.[2] Surprisingly, there are few reports of the lithiation of 1,1-dibromo-2-trialkylsilylcyclopropanes, although reaction of the parent compound **1** (R = H) with butyllithium at low temperature has been found to produce 1-bromo-2-trimethylsilylcyclopropyllithium. This may be trapped by addition to a ketone, although reported yields are not high.[3] We now report that reaction of such compounds with methyllithium at −90 to 20 °C leads to a cyclopropene.

1,1-Dibromo-2-alkyl-2-trialkylsilylcyclopropanes **1** are available in two steps from 2-bromoalkenes, by formation of a Grignard reagent and trapping with a trialkylsilyl chloride, and then dibromocyclopropanation using aq. sodium hydroxide, bromoform and cetrimide under phase transfer catalysis conditions. Treatment of **1** with methyllithium at −90 °C followed by warming to −50 °C or at 20 °C, in each case quenching with water at that temperature, leads to the corresponding 1-alkyl-2-trialkylsilylcyclopropene; the reaction is successful with 1.1 mol equiv. of the alkyllithium, though an excess is normally used. In this way **1** (R = Bu) is converted into **2** (R = Bu) (82%) at 20 °C (Scheme 1).†

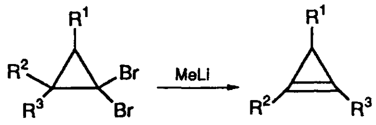


1 **2** **3**

Scheme 1

In the same way, the dibromides shown in Table 1 are each converted into the corresponding cyclopropene. These reactions may be explained in terms of a 1,2-shift in an intermediate carbene (carbenoid), **3**. Such 1,2-shifts are rare in cyclopropylidenes, although examples have been reported.[8] In the present case it seems likely that the migrating group is R_3Si rather than hydrogen or alkyl; thus, alkyl group migrations are not reported in the reactions of a large number of alkyl-substituted cyclopropylidenes, while silyl groups are known to undergo very rapid shifts in other systems. It is interesting that a trimethylsilyl shift in a 1-trimethylsilyl-2-methylthiocyclopropene has been reported to lead to a vinylcarbene,[9] while 1-trimethylsilyl-3,3-dimethylcyclopropene is reported to ring open thermally to produce a methylenecarbene,[10] and that the activation parameters for 1,3-silicon shifts in 3-trialkylsilylcyclopropenes have been determined.[11]

Table 1 Reaction of 1,1-dibromides with methyllithium at 20 or −90 °C



R^1	R^2	R^3	Yield	(%)
			A	B
			(20 °C)	(−90 °C)
H	Bu	$SiMe_3$	82	73
H	Oct	$SiMe_3$	86	94
H	Me	$SiMe_2Ph$	84	93
H	Oct	$SiMe_2Ph$	94	62
Me	Me	$SiMe_2Ph$	72*	
H	H	$SiMe_3$	48[6,†]	

* The cyclopropane was obtained as a mixture of stereoisomers, but on reaction with methyllithium a single cyclopropene was obtained.

† After trapping with diphenylisobenzofuran; the product showed δ_H −0.31 (9 H, s), 1.26 (1 H, dd, *J* 6.3, 4.8), 1.77 (1 H, dd, *J* 6.3, 3.5), 2.11 (1 H, dd, *J* 4.8, 3.5), 7.02–7.07 (1 H, complex m), 7.11–7.2 (2 H, complex m), 7.21–7.26 (1 H, complex m), 7.36–7.47 (6 H, m), 7.62–7.69 (2 H, m) and 7.75–7.79 (2 H, m).

Experimental

Methyllithium (1.04 mmol) in diethyl ether was added slowly dropwise to a solution of 1,1-dibromo-2-butyl-2-trimethylsilylcyclopropane (0.3 g, 0.92 mmol) in dry diethyl ether (5 cm^3) at room temperature under an atmosphere of argon; this caused a temperature rise of *ca.* 10 °C. The reaction mixture was stirred at room temperature for 1 h, after which water (1 cm^3) was added to quench any excess of methyllithium. The aqueous and organic layers were separated. The aqueous layer was extracted with diethyl ether (3 × 10 ml) and the combined ethereal layers washed with water (1 × 10 cm^3), dried ($MgSO_4$) filtered and evaporated at 14 mmHg to give a crude product which was purified by flash distillation at < 0.05 mmHg to give *2-butyl-1-trimethylsilylcycloprop-1-ene* **2** (R = Bu) as a yellow oil (0.13 g 82.0% at room temperature); ν_{max}/cm^{-1} 2958s, 2875s, 1797s, 1466m, 1379w, 1248s, 1100w, 992m and 840s; δ_H 0.17 (9 H, s), 0.73 (2 H, s), 0.94 (3 H, t, *J* 7.2), 1.25–1.65 (4 H, complex multiplet), 2.56 (2 H, t, *J* 7.2); δ_C −1.3, 6.2, 13.8, 22.4, 28.2, 29.4, 104.9 and 135.3.

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† 1-Trimethylsilylcyclopropenes have been obtained by a variety of routes including the reaction of cyclopropenyllithium with trimethylsilyl chloride,[4,5] the addition of carbenes to mono- and bis-(alkylsilyl)-alkynes,[6] the cyclisation of 1,3-diiodoalkenes,[7] and the dehalogenation of 1,1,2-trihalogeno-2-trimethylsilylcyclopropanes.[2]

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References

1 See *e.g.*, J. Backes and U. H. Brinker, in *Methoden der Organischen Chemie*, E19b, vol. 2, Houben-Weyl, 1989, 391–510.

2 See *e.g.*, B. R. Dent, B. Halton and M. F. Smith, *Aust. J. Chem.*, 1986, **39**, 1621.

3 A. Weber, R. Galli, G. Sabbioni, U. Stampfli, S. Walther and M. Neuenschwander, *Helv. Chim. Acta*, 1988, **71**, 2026; 1989, **72**, 41; G. Sabbioni, A. Weber, R. Galli and M. Neuenschwander, *Chimia*, 1981, **35**, 95; see also P. Engel, C. Lang, M. Muhlebach and M. Neuenschwander, *Chimia*, 1992, **46**, 381.

4 See *e.g.*, I. B. Avezov, I. G. Bolesov and R. Y. Levina, *Zh. Org. Khim.*, 1974, **10**, 2114.

5 M. S. Baird, H. H. Hussain and W. Nethercott, *J. Chem. Soc., Perkin Trans. 1*, 1986, 1845.

6 See *e.g.*, Y. V. Tomilov, A. B. Kostitsyn, E. V. Shulishov and O. M. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1141.

7 A. T. Stoll and E. Negishi, *Tetrahedron Lett.*, 1985, 5671; E. Negishi, L. D. Boardman, H. Sawada, V. Bagheri, A. T. Stoll, J. M. Tour and C. L. Rand, *J. Am. Chem. Soc.*, 1988, **110**, 5333.

8 See *e.g.*, A. Oku and K. Yagi, *J. Am. Chem. Soc.*, 1974, **96**, 1966. 1,3-Di-*tert*-butylcyclopropene has been reported to be a minor product from the reaction of 2,3-di-*tert*-butylcycloprop-l-ylidene, presumably by a 1,2-hydrogen shift (F. D. Green, R. L. Camp, V. P. Abegg and G. O. Pierson, *Tetrahedron Lett.*, 1973, 4091).

9 R. Walsh, C. Wolf, S. Untiedt and A. de Meijere, *J. Chem. Soc., Chem. Commun.*, 1992, 422.

10 See *e.g.*, E. Colvin, Silicon in Organic Synthesis, Butterworths, London, 1981; A. Sekiguchi and W. Ando, *Chem. Lett.*, 1983, 871; X. Creary and Y.-X. Poon, *Tetrahedron Lett.*, 1989, 2493; J. J. W. McDonald, H. B. Schlegel and J. S. Francisco, *J. Am. Chem. Soc.*, 1989, **111**, 4622.

11 B. Coleman, N. D. Conrad, M. W. Baum and M. Jones, *J. Am. Chem. Soc.*, 1979, **101**, 7743.

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