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Reactions of 1,2-Dihalocycloalkenes with Alkali Metals in Presence of Chlorotrimethylsilane. Reductive Carbon-Carbon Bond Cleavage in Five Membered Homocyclic System[1]

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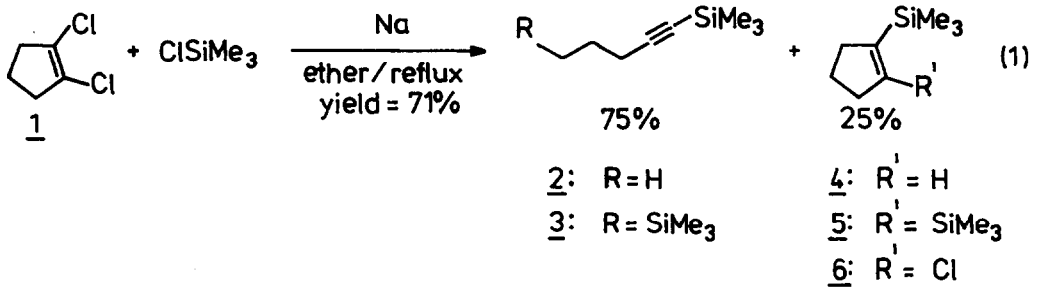
Key Words: Vinylsilanes; dihalocyclopentenes; halocyclopentenyl anions; homocyclic ring cleavage; alkynylsilanes.

Abstract: 1,2-Dihalocyclopentenes on reaction with alkali metals and chlorotrimethylsilane in hydrocarbon or ether solvents produce silylated 1-pentynes by ring opening. Sodium metal and hydrocarbon solvents favour the cleavage most. Different mechanistic aspects are considered.

INTRODUCTION

It has been known for a long time that 1,2-dibromocycloalkenes undergo debromination with alkali metals or magnesium to give cycloalkynes.[2] We discovered that 1,2-dichlorocyclopentene (**1**) reacts with sodium in the presence of chlorotrimethylsilane (TMS-Cl) to give, instead, essentially ring opened products, the 1-pentyne

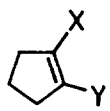


derivatives **2** and **3** (eq 1) along with minor amounts of **4**, **5** and **6**, but none of the cyclopentyne trimer **7**.[3] Neither the dihalocyclopentenes on reaction with sodium,[2] nor the 2-halocyclopentenyl-1-anions of the type **8** and **9**, which are intermediates in the former reactions[4] and which could be independently prepared by the reactions of alkyllithiums with dihalocyclopentenes,[5] are reported to produce any ring opened product. It was felt desirable to look into this unusual homocyclic ring cleavage process more closely concerning its scope and mechanism. This paper deals with some of these aspects.

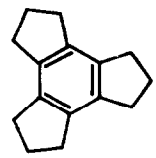
RESULTS

1,2-Dichlorocyclopentene (**1**) underwent ring opening,[3] to give **2** and **3** that constituted about 75% of the product (eq 1). The silylated pentynes **2**[6] and **3** were identified by their spectral properties and by independent synthesis from 5-chloro-1-pentyne. On catalytic hydrogenation, **2** and **3** absorbed two molar equivalents of hydrogen each and produced respectively 1-trimethylsilylpentane[7] and 1,5-bis(trimethylsilyl)pentane.

The monohalocyclopentenes **6, 10-12,** and 1,2-dichlorocyclohexene (**14**) have previously been shown not to produce any ring cleavage products under similar conditions.[3,8] Now, it is observed that **13** also does not give any ring opened products.



10: X = H, Y = Cl
11: X = H, Y = Br
12: X = CH_3, Y = Cl
13: X = Br, Y = $SiMe_3$
15: X = Y = Br
16: X = Br, Y = Cl
32: X = CH_3, Y = $SiMe_3$



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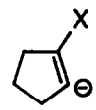
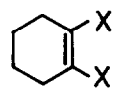


8: X = Cl
9: X = Br



14: X = Cl
17: X = Br

It was therefore necessary to elicit the essential structural features in the substrates that would induce the ring cleavage. The previous results[3,8] suggested that, for the successful ring cleavage, the substrate may have to be a 1,2-dihalosubstituted cyclopentene. The dibromo-analogue **15** was therefore prepared and was reacted under the same condition. However, it produced only 20% of the ring opened products and **4, 5** and **13**, but no cyclopentyne trimer **7** was observed. It maybe noted that Favorsky isolated only **7** when **15** was reacted directly with sodium in ether.[9] Hence, we thought that, for successful ring opening, the halogen on C-2 must be chlorine rather than bromine as in **8**, but not **9**. To verify this, 1-bromo-2-chlorocyclopentene (**16**) was prepared and reacted with sodium and TMS-Cl in ether at 50° C. However, in this case also the total amount of the pentynes **2** and **3** obtained was only about 16% of the products. Therefore, it seemed necessary that Cl or Br should be present on C-2 of the cyclopentenyl anion as in **8** and **9** but that was not enough to bring about ring cleavage. More important, it appeared that prior to the formation of **8** the presence of chlorine and not bromine on C-1 that was responsible for the successful ring opening. It was thought that the formation of low proportion of ring cleavage products from **15** and **16** was due to the inadequacy of the reaction conditions, and suitable variations of temperature, solvent and metal were considered for bringing about the desired effect. Each of these parameters was varied and the solvent was found to influence the course of the reaction tremendously. The results of the variation in each case are described below.

Effect of temperature

When the reaction was carried out in ether at room temperature (rt) instead of 50° C, **1** did not show any tendency to react. However, both **15** and **16** reacted slowly at rt to give **2** and **3** in the same proportion as they did

at 50-55° C. At higher temperatures tarry material resulted.

Effect of solvent

Reactions were run in ether, tetrahydrofuran (THF), benzene, cyclohexane and cyclohexene to examine the effect of solvent polarity. The dihalides **1** and **16** reacted with sodium and TMS-Cl significantly faster in THF than in ether, but **15** reacted at about the same rate, and the proportion of ring cleavage products remained at about the same respective level as in ether (Table I). However, when the solvent was changed to a hydrocarbon like benzene or cyclohexane, a dramatic increase in the proportion of the ring cleavage products from both **15** and **16** was observed. Even **1** produced higher proportion of the pentynes **2** and **3**, particularly in cyclohexane, than it did in ether or THF when either sodium or potassium was used (Table I). Reactions run in cyclohexene as solvent also yielded results similar to those obtained in cyclohexane and benzene.

Table I. Reaction of 1,2-Dihalocyclopentenes with Metal and TMS-Cl

compd	metal	solvent	temp, °C	time, h	total ring opened product (2 + 3),[b] %	total silylated cyclopentenes[a] (4 + 5 + 6), [b] %
1	Na	ether	50	60	71-75	21-25
	Na	THF	55	16	54-56	46-49
	Na	benzene	55	10	70-76	25-28
	Na	cyclohexane	55	10	67-73	22-27
	K	ether	30	13	20-22	54-58
	K	THF	30	3	0-5	90-95
	K	benzene	30	2	23-27	59-63
	K	cyclohexane	30	5	38-42	51-55
	Mg	THF	60	350	35-40	—
15	Na	ether	50	12	16-20	74-80
	Na	THF	55	12	8-13	87-92
	Na	benzene	55	6	48-50	35-38
	Na	cyclohexane	55	8	59-62	24-26
	K	ether	30	2.5	32-36	53-55
	K	THF	30	3	12-15	70-73
	K	benzene	30	2.5	34-39	40-42
	K	cyclohexane	30	2.5	21-23	47-49
	Mg	ether	60	85	< 1	67-73
	Mg	THF	60	60	10-11	85-88
16	Na	ether	50	60	13-16	81-84
	Na	THF	55	16	9-10	84-89
	Na	benzene	55	5	48-53	22-28
	Na	cyclohexane	55	5	64-71	23-26
	Na	cyclohexene	55	5	64-67	22-24
	K	ether	30	4	24-27	54-59
	K	THF	30	4	< 1	81-86
	K	benzene	30	1	22-25	44-47
	K	cyclohexane	30	1	25-27	50-52
	Mg	THF	60	100	< 1	98

[a] These are results of 5 to 10 runs in each solvent using Na or K as metal and 3 runs using Mg. [b] The ratio of **2**:**3** may vary widely, (which seems to depend on the level of dryness of the solvent), but their total quantity remains within the range given. The same is the case with the ratio of **4**, **5** and **6** (or **13**). When the reaction is prolonged **6** (or **13**) is converted essentially to **5**. (The formation of protonated products **2** and **4** in spite of the presence of excess TMS-Cl is not quite clear).

Effect of metals

The dihalocyclopentenes **1**, **15** and **16** reacted with potassium at room temperature, but produced lower proportions of ring cleavage products (Table I). Lithium was unsatisfactory, as no reaction occurred below 60° C and decomposition was observed at higher temperatures. Magnesium reacted with **1** and **16** in THF and with **15** in both ether and THF, to yield some ring opened products (Table I).

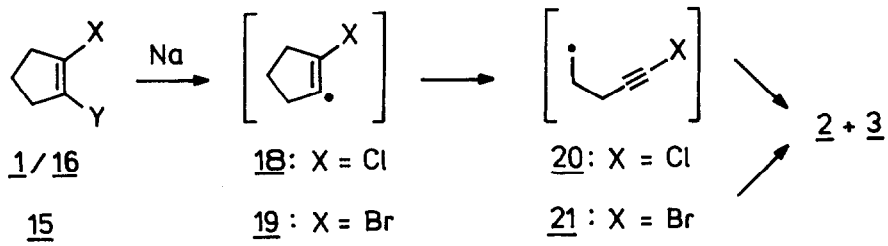
Effect of ring size

Both 1,2-dichlorocyclohexene (**14**) and its dibromo-analogue **17** reacted with sodium and TMS-Cl in ether, THF, benzene and cyclohexane to give complex mixtures of products, which showed no IR band between 2100 and 2200 cm^{-1} indicating no formation of 1-hexyne derivative.

DISCUSSION

The results establish that, in order for the ring cleavage to occur, both C-1 and C-2 positions of the cyclopentene ring should be substituted by halogens. Only one halogen, as in **6** and **10-13** is not sufficient, even if the other group is bulky (e.g. **6** and **13**), to cause ring opening.

The reaction would be initiated by the transfer of electrons from the metal to carbon-halogen bond leading to the formation of the radical **18/19** by one electron transfer[10] (Scheme I) or to the anion **8/9** by two electron transfer. The following evidence however, is against the radical mechanism depicted in Scheme I. First, the reaction of **16** with tri-n-butyltin hydride[11] in the presence of 2,2'-azobisisobutyronitrile (AIBN) produced only 1-chlorocyclopentene (**10**)



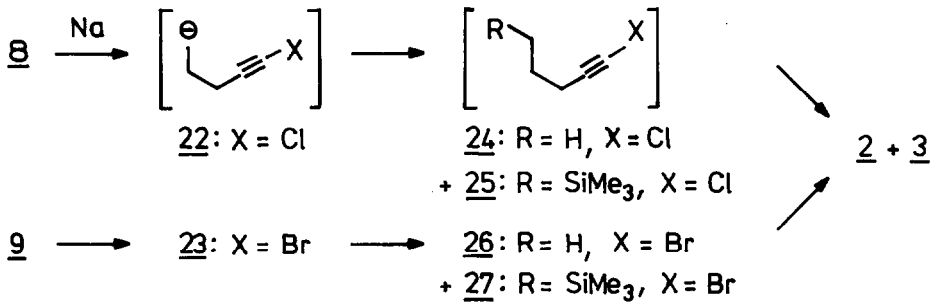
Scheme I

without a trace of 1-chloro-1-pentyne (**24**), indicating that the radical **18** is formed on reaction of **16** with tri-n-butyltin hydride, but that it does not undergo ring cleavage. Secondly, the proportion of ring cleavage is greatly influenced by the polarity of the solvent (Table I) as also the added salt (NaBr) (Table II). This clearly indicates that the reaction takes an ionic rather than a radical course.[12] The intermediacy of the anion **8/9** is further indicated by the isolation of **6** and **13** from the reactions of **1**, **15** and **16**. There are also literature reports on the characterization of the anion **9** with Li^+ as counterion.[5]

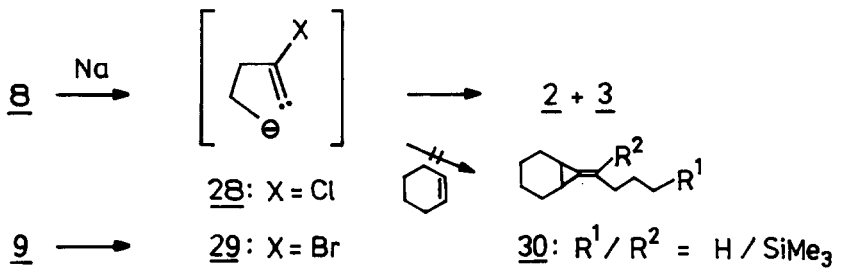
Table II: Effect of NaBr on Cleavage of 1 with Na-TMS-Cl

qty of NaBr (mol eq)	solvent	temp, °C	time, h	(2 + 3),%	(4 + 5 + 6),%
1	THF	55	19	33	67
2	THF	55	21	26	74
4	THF	55	23	19	81
7	THF	55	20	15	83
2	ether	50	55	53	47
7	ether	50	55	51	43

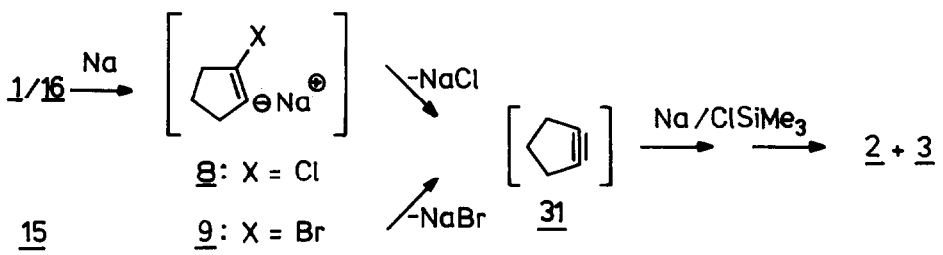
Once the anion **8/9** is formed, it can be visualized to undergo ring cleavage directly by C_2-C_3 bond breaking (Scheme II) or through the vinyl carbene **28/29** by C_1-C_5 bond breaking (Scheme III) or through cyclopentyne (**31**) which due to enormous strain would open up to give the acyclic products (Scheme IV).



Scheme II



Scheme III

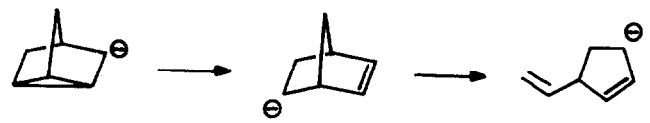


Scheme IV

The formation of cyclopentyne was not observed by usual trapping procedures. For example, trapping experiments using diphenylisobenzofuran and tetracyclone for [4+2] addition, [2b, 5a] and cyclohexene for [2+2] addition[13] did not produce any expected cycloaddition product. Similarly, the trimer **7**,[14] which is considered to be an important proof for the formation of cyclopentyne, [4a, 4b] was also not observed.

The reaction in cyclohexene also failed to produce any carbene addition product **30** (Scheme III) that was expected if the vinyl carbene **28/29** were to be formed by the C_1-C_5 bond cleavage.[15] In fact, the results obtained in cyclohexene as solvent were very much similar to those in cyclohexane (Table I).

In the absence of any positive proof for the formation of either cyclopentyne (**31**) or vinyl carbene **28/29**, it is presumable that direct cleavage of the C_2-C_3 bond of the anion **8/9** takes place (Scheme II) to give the observed products. If indeed the ring opens immediately after the formation of the anion **8/9**, then it would be an unprecedented case of carbacyclic ring opening of an "endocyclic" anion. There are instances of homocyclic ring opening reactions mediated by "exocyclic" anions such as in equations 2,[16] 3,[17] 4,[18] and 5 (Haller Bauer cleavage).[19] There are also examples of cleavage of heterocycles with endocyclic or exocyclic anions (eq 6 and 7).[20] The driving force for such ring opening reactions is believed to be relief of ring strain and/or stabilization of the leaving group.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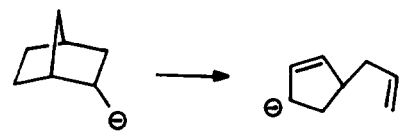
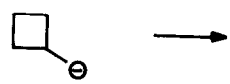
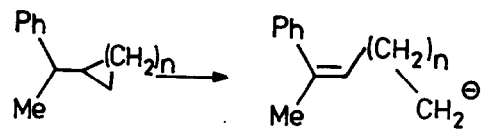

(3)


(4)


(5)


(6)


(7)

The destabilizing effect in **8/9** may not be due to the ring size alone, since compounds **6** and **10-13**, which would be expected to form the anions, however, did not produce any ring cleavage product, but produced only the silylated cyclopentenes **5**, **4**, **4**, **32** and **5** respectively.[3,8] On the other hand, the presence of a halogen adjacent to the carbanion centre is not enough since dichloro- and dibromo-cyclohexenes **14** and **17** did not give ring opened products. Therefore, the cleavage seems to be brought about by a combination of these two effects, namely (i) the ring size and (ii) the presence of a halogen next to the carbanion.

The occurrence of larger proportion of ring cleavage products with sodium metal in hydrocarbon solvents indicates that these reactions involve tight ion pairs (compared to the situation in ether or THF) of **8/9** with counterion Na^+ providing **8/9** a longer lifetime and consequently a better chance for it to undergo structural changes.[19,21] This ion pair concept also explains neatly why **15** and **16** gave similar results, but **1** yields higher proportion of cleavage products. The bromide ions formed in the reactions of **15** as well as **16** would cause some loosening of the tight ion pairs and reduce the lifetime of **8**, whereas the chloride ions formed in the reaction of **1** are not as effective in causing sufficient seperation of the ion pair to reduce the lifetime of **8**. Evidence for this assumption was obtained by adding sodium bromide to the reaction of **1** in THF, when a steady decrease in the proportion of ring cleavage products was noted as increasing amounts of NaBr was added (Table II). This common ion effect was not observed in benzene.

Attempts to detect the possible intermediate halopentynes **24-27** at various intervals of time during the reactions of **1** and **16** were unsuccessful. Halopentynes **24-27** do not seem to be stable enough to be detected under the reaction conditions, since **24** prepared independently[22] reacted almost instantaneously when subjected to the same reaction conditions to produce **2**.[23]

In conclusion, the results demonstrate that reductive ring cleavage is a general reaction of 1,2-dihalocyclopentenes, if suitable conditions are provided. Four possible routes have been considered for the conversion of 1,2-dihalocyclopentenes to 1-pentynes. The free radical route seems to be unlikely. It seems certain that 2-halo-1-cyclopentenyl anion **8/9** is an intermediate, and it is likely that this opens directly as no other subsequent intermediate could be detected.

EXPERIMENTAL SECTION

Instruments

^{1}H NMR spectra were recorded on JEOL FX-90 Q and Bruker AC-250 spectrometers and the chemical shifts are relative to $CHCl_3$ (δ 7.27) for compounds with -$SiMe_3$ group (whether or not TMS is added), and to TMS for those without -$SiMe_3$ group. ^{13}C NMR spectra were recorded on Bruker AC-250 instrument and the chemical shifts are relative to $CDCl_3$ for compounds with -$SiMe_3$ group. IR spectra were run on Beckmann IR-4260 and Carl Zeiss Specord-75 spectrophotometers with films of liquid samples between NaCl plates. GC-MS were obtained on HP 5985 B system attached to HP 5840 A gas chromatograph. GC analysis were carried out on Shimadzu GC-6 A and Varian Vista 6000 instruments on 10% OV 101, 15% FFAP and 3% nitrilesilicone oil columns with temperature programmes. Preparative GC was performed using Perkin-Elmer F-21 instrument.

Materials

The dihalocycloalkenes **1**,[24] **14**,[25] **15**,[9,26] and **17**,[27] were prepared according to literature procedures. Solvents used for silylation reactions were refluxed on sodium and benzophenone and distilled before use. TMS-Cl was distilled over finely cut sodium.

1-Bromo-2-chloro-1-cyclopentene (16)

Bromine chloride[28] (48 g, 0.42 mol) was prepared by adding a solution of 33 g (0.21 mol) of bromine in 50 mL of CCl_4 at 0° C to a solution of 15 g (0.21 mol) of chlorine in 100 mL of CCl_4 at 0° C. The mixture was cooled to -15° C with stirring and a solution of 20.0 g (0.195 mol) of 1-chlorocyclopentene in 25 mL of CCl_4 was added dropwise over a period of 1 h. Immediately after the addition was completed, the excess halogens were destroyed by careful addition of saturated $NaHSO_3$ solution. The layers were separated, the organic layer was washed with $NaHSO_3$ solution (100 mL), water (50 mL), NaCl solution (25 mL), dried ($MgSO_4$), and concentrated. The residue was distilled (85-88° C/5.0 Torr) to get 20.3 g (47.5%) of 1-bromo-2,2-dichlorocyclopentane, which without further purification, was added during 2 h to a solution of 20g (0.35 mol) of KOH in 150 ml of 96% ethanol with stirring and the mixture was refluxed for 12 h. After cooling, 250 mL of $CHCl_3$ was added followed by 100 ml of water. The layers were separated, the aqueous layer was extracted with chloroform (5 x 200 mL), the combined organic extracts were washed with water (5 x 100 mL) and brine (2 x 200 mL), dried over $MgSO_4$, concentrated and the residue distilled under reduced pressure. Bromochlorocyclopentene **16** was collected at 62° C/9 Torr, yield, 6.8 g (40%); **IR** 2930, 2860, 1620, 1590, 1420, 860, 630 cm^{-1}; **^{1}H NMR** ($CDCl_3$) δ 2.55 (m, 4H), 2.02 (m, 2H); **MS** m/e (relative intensity) 184 (1), 182 (6), 180 (5) (M^+), 147 (5), 145 (5) (M^+-Cl), 103 (10), 101 (37) (M^+-Br), 65 (100), 39 (66); (Found: C, 33.37; H, 3.41. C_5H_6BrCl requires C, 33.09; H, 3.31).

Reaction of 1,2-dichlorocyclopentene (1) with sodium and TMS-Cl

To a suspension of 3.01 g (130.8 mmol) of finely cut sodium in 40 mL of ether in a 100-mL round bottomed flask fitted with a condenser and a dropping funnel, kept preferably under nitrogen atmosphere or protected by $CaCl_2$ guard tube, were added 8.30 g (76.4 mmol) of TMS-Cl and 3.46 g (25.2 mmol) of 1,2-dichlorocyclopentene (**1**). The mixture was refluxed with efficient cooling on an oil bath at 50-55° C. The reaction was followed by GC and was found to require 45-50 h for its completion. The mixture was cooled, the precipitated solids and the remaining sodium were removed by passing through a plug of glass wool and washed with ether (2 x 5 mL). Water (40 mL) was carefully added to the combined filtrate, the layers were separated, the organic layer was successively washed

with water (3 x 40 mL), 10% aqueous $NaHCO_3$ (50 mL), water (40 mL), saturated aqueous NaCl (40 mL), dried ($MgSO_4$) and concentrated to get 2.87 g of crude product. GC on 3 m 3% XE 60 (nitrilesilicone oil) column with temperature programme of 60 to 180° at 4°/min using nitrogen as carrier gas (30 mL/min), showed **2** (9%, t_R = 4.6 min), **4** (6%, 5.1 min), **5** (3%, 9.8 min), **6** (11%, 11.6 min), **3** (62.5%, 12.8 min) and several small peaks at higher retention times.

The compounds **2**, **3**, and **6** were isolated by preparative GC; (samples of **2**, **3** and **6** were also prepared independently, see below); **2**: bp 123-125° (Lit[4] bp 55-57° C/35 Torr); **IR** 2960, 2930, 2900, 2870, 2175, 1250, 980, 840, 760 cm^{-1} ; **^{1}H NMR** ($CDCl_3$) δ 0.17 (s, 9H), 0.77 (t, J = 7.8 Hz, 3H), 1.39 (sextet, J= 7.5 Hz, 2 H), 2.20 (t, J = 7.5 Hz, 2H); **^{13}C NMR** ($CDCl_3$) δ 0.4, 13.6, 22.0, 22.3, 84.7, 107.7; **MS** m/e (relative intensity) 140 (10), 126 (12), 125 (100), 97 (7), 96 (6), 83 (10), 81 (6), 73 (6), 69 (5), 59 (5), 53 (5), 43 (7); **3**: bp 62°/0.5 Torr; **IR** 2955, 2930, 2900, 2875, 2175, 1250, 1025, 890, 840, 760, 695, 640 cm^{-1}; **^{1}H NMR** ($CDCl_3$) δ 0.0 (s, 9H), 0.15 (s, 9H), 0.59 (m, 2H), 1.54 (m, 2H), 2.23 (t, J = 7 Hz, 2H); **^{13}C NMR** ($CDCl_3$) δ -1.8, 0.3, 16.4, 23.6, 23.7, 84.5, 107.8; **MS** m/e (relative intensity) 212 (0.1), 198 (3), 197 (14), 184 (5), 171 (3), 170 (8), 169 (41), 155 (3), 141 (3), 124 (3), 123 (6), 109 (4), 101 (20), 97 (7), 96 (19), 83 (7), 81 (10), 74 (9), 73 (100), 69 (4), 67 (3), 59 (14), 45 (25), 43 (7); (Found: C, 62.41; H, 11.20. $C_{11}H_{24}Si_2$ requires C, 62.26; H, 11.32%); **6**: for spectral and other data, see separate preparation of **6**, below.

Reactions of other dihalocycloalkenes, and reactions using other metals and solvents

Reactions of all the dihalocycloalkenes in various solvents and using different metals involved the same sequence of steps as described for the reaction of **1** with sodium and TMS-Cl in ether. Other experimental conditions like temperature and duration of reaction are given in Table I. The amount of dihalocycloalkene taken varied from about 100 mg to slightly more than 3 g. This does not affect the results. Normally, 3-4 equivalents of TMS-Cl and 6-7 equivalents of metal were used (if lower proportions of these reactants were used the reaction stopped from proceeding to completion).

Hydrogenation of 2 and 3

A mixture of 0.20 g of the product of the reaction of **1** (fraction bp 55-65 /4 Torr, slightly enriched with **2**, but still containing **2**-**6**) and 8 mg of 5% palladium-on-charcoal catalyst in 5 mL of distilled methanol was stirred in a 25-mL flask under hydrogen atmosphere for 30 min by which time **2** and **3** had disappeared. The catalyst was filtered off, the filtrate was taken up in 20 mL of ether, the solution was washed with water (3 x 15 mL), aqueous NaCl (15 mL) dried ($MgSO_4$) and concentrated. Through preparative GC (3 m 5% OV-101 glass column, 80 to 150 at 5 /min) two compounds corresponding to hydrogenated **2** and **3** were isolated. First component (CH_3-CH_2-CH_2-CH_2-CH_2-$SiMe_3$):[7] **IR** 2975, 2965, 2880, 2850, 1410, 1260, 1255, 840, 755 cm^{-1}; **^{1}H NMR** ($CDCl_3$) δ 0.02 (s, 9H), 0.51 (m, 2H), 0.91 (m, 3H), 1.31 (m, 6H); **MS** m/e (relative intensity) 144 (2), 129 (47), 101 (3), 87 (5), 73 (100), 59 (17), 45 (4). Second component (Me_3Si-CH_2-CH_2-CH_2-CH_2-$SiMe_3$): **IR** 2980, 2965, 2880, 2855, 1415, 1265, 1255, 915, 840, 760, 695 cm^{-1}; **^{1}H NMR** ($CDCl_3$) δ 0.02 (s, 18H), 0.49 (m, 4H), 1.33 (m, 6H); **MS** m/e (relative intensity) 216 (0.5), 201 (3), 127 (12), 113 (57), 99 (52), 85 (19), 73 (100), 59 (15), 45 (21), 43 (5); (Found C, 61.13; H, 13.08. $C_{11}H_{28}Si_2$ requires C, 61.02; H, 13.03).

1-Chloro-2-trimethylsilylcyclopentene (6)

To a stirred suspension of 2.12 g (92.2 mmol) of finely cut pieces of sodium in 10 mL of THF were added 7.70 g (70.9 mmol) of TMS-Cl and 5.02 g (27.5 mmol) of **16**. The mixture was stirred at room temperature for 2 h and worked up. The product was fractionally distilled to obtain 3.05 g (63.6%) of **6**, bp 50-52° C/4 Torr; **IR** 2960, 2900, 2850, 1600, 1440, 1410, 1310, 1250, 1050, 905, 840, 740, 700, 630 cm^{-1}; **^{1}H NMR** ($CDCl_3$) δ 0.17 (s, 9H), 1.91 (quintet, J = 7.8 Hz, 2H), 2.45 (t, with fine splitting, 2H), 2.60 (t, with fine splitting, 2H); **MS** m/e (relative intensity) 176 (6), 174 (16), 161 (12), 159 (32), 133 (52), 131 (14), 123 (9) 119 (3), 117 (5), 105 (5), 103 (7), 97 (3), 96 (4), 95 (40), 93 (100), 81 (18), 80 (12), 79 (13), 73 (36), 67 (5), 66 (8), 65 (13), 63 (10), 53 (4); (Found: C, 55.14; H, 8.49. $C_8H_{15}ClSi$ requires C, 54.99; H, 8.65).

1-Bromo-2-trimethylysilylcyclopentene (13)

A mixture of 0.82 g (35.7 mmol) of finely cut sodium, 1.88 g (17.3 mmol) of TMS-Cl and 2.01 g (8.9 mmol) of **15** was stirred at room temperature for 2 h. Usual work up and fractional distillation of the product yielded 1.28 g (65.9%) of **13**, bp 48° C/1.5 Torr; **IR** 2950, 2900, 2850, 1600, 1250, 1070, 1025, 825, 760 cm^{-1}; **^{1}H NMR** ($CDCl_3$)

δ 2.66 (m, 2H), 2.42 (m, 2H), 1.84 (quintet, J = 7.7 Hz, 2H), 0.20 (s, 9H); **MS** m/e (relative intensity) 220 (12), 218 (12), 205 (31), 203 (30), 139 (99), 137 (97), 73 (100); (Found: C, 43.64; H, 6.79. $C_8H_{15}BrSi$ requires C, 43.83; H, 6.89).

1,2-Bis(trimethylsilyl)cyclopentene (5)

A mixture of 0.05 g (2.2 mmol) of finely cut sodium, 1.21 g (11.1 mmol) of TMS-Cl and 0.22 g (1.0 mmol) of **13** in 10 ml of ether was refluxed on an oil bath at 40-45° C for 24 h and then worked up. Distillation of the product provided 0.10 g (47.1%) of pure **5**, bp 52-55° C/2 Torr; **IR** 2980, 2900, 2850, 1390, 1230, 1080, 970, 780 cm^{-1}; **^{1}H NMR** ($CDCl_3$) δ 2.60 (t, J = 7.7 Hz, 4H), 1.65 (quintet, J = 7.7 Hz, 2H), 0.22 (s, 18H); **MS** m/e (relative intensity) 212 (3), 197 (7), 169 (16), 124 (19), 109 (8), 96 (10), 73 (100), 59 (23), 45 (47); (Found: C, 62.28; H, 11.43. $C_{11}H_{24}Si_2$ requires C, 62.26; H, 11.32).

Reaction of 16 with tri-n-butyltin hydride

To a mixture of 0.27 g (1.5 mmol) of **16** and 0.04 g (0.3 mmol) of AIBN in 1 mL of dry tert-butyl alcohol stirred under nitrogen atmosphere was added 0.92 g (3.2 mmol) of tri-n-butyltin hydride through a syringe. The mixture was refluxed (on an oil bath at 80° C) and the progress of the reaction was followed by GC analysis, which indicated that **16** had reacted completely in 1 h with the formation of chlorocyclopentene (**10**) exclusively, which was isolated (by adding the product mixture to water, extracting with CH_2Cl_2, and distilling the product after removing the solvent, yield 92%) and its identity confirmed by comparing its physical and spectral characteristics with those of authentic sample and converting it into 1,2-dibromo-1-chlorocyclopentane.

The reaction was repeated using dry toluene as solvent and the product obtained was again **10** only, (yield 84%).

Preparation of 2 and 3 from 5-chloro-1-pentyne

A mixture of 1.51 g (65.6 mmol) of finely cut sodium, 3.25 g (29.9 mmol) of TMS-Cl and 1.03 g (10.0 mmol) of 5-chloro-1-pentyne (Aldrich) in 20 mL of ether was refluxed for 30 h and worked up in the usual way. The product contained essentially two components in about 1:3 ratio which were separated by preparative GC, and found to possess retention times (coinjection) and spectra (NMR, IR and MS) identical with those of **2** and **3** obtained from **1**, **15** and **16**.

Reaction of 1-chloropentyne with Na and TMS-Cl

1-Chloropentyne,[22] **24**, (0.15 g, 1.4 mmol) in 2 mL of ether was added dropwise over 5 min into a mixture of 0.21 g (9.1 mmol) of finely cut sodium and 0.34 g (3.1 mmol) of TMS-Cl in 5 mL of dry ether stirred and refluxed under nitrogen. The mixture was further refluxed for 5 min and worked up to obtain 0.10 g (51%) of a product which was identified as **2**.

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