# 1-Trimethylsilylbuta-1,3-dienes and 1-Trimethylsilylbicyclo[1.1.0]-butanes from 1,1,1-Tribromobut-3-enes†

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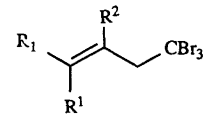
Reaction of 1,1,1-tribromobut-3-enes with butyllithium at −110 °C leads to lithium–bromine exchange to generate 1,1-dibromo-1-lithiobut-3-enes which may be trapped by trimethylsilyl chloride to produce 1,1-dibromo-1-trimethylsilylbut-3-enes. These are converted into (*Z*)-1-bromo-1-trimethylsilylbuta-1,3-dienes by reaction with diazabicyclo[5.4.0]undec-7-ene and into 1-trimethylsilylbicyclo[1.1.0]butanes by reaction with methyllithium.

Dedicated to Professor Lars Skattebøl on the occasion of his 65th birthday.

The reaction of allylic bromides with bromoform and aqueous sodium hydroxide in the presence of certain phase-transfer catalysts has been shown to lead to 1,1,1-tribromobut-3-enes (**1**) in a reaction which probably involves displacement of bromide ion by tribromomethanide.[2] In this paper we describe the conversion of these tribromides to the corresponding silanes (**2**), and the transformation of these into synthetically useful 1-trimethylsilylbuta-1,3-dienes (**3**) and to bicyclobutanes (**4**).

Treatment of the tribromide **1a** in ether, tetrahydrofuran and pentane at −115 °C with butyllithium followed by trimethylsilyl chloride led to the silane (**2a**) (69 %), which showed a typical pattern for the allyl group in its $^1$H NMR spectrum, together with a nine-hydrogen singlet for the silyl-group. In the same way, **1b** and **1c** gave **2b** and **2c** in 64 and 50 % yield, respectively. These reactions apparently proceed by lithium–bromine exchange to produce **5**, X = Li, which is trapped by the added electrophile;[3] in agreement with this, treatment of **1b** with butyllithium at −115 °C as above and quenching with water, ethyl acetate or allyl bromide led to **5b**, X = H, COMe, $CH_2CH{=}CH_2$, respectively.



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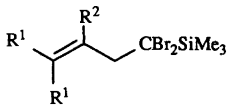

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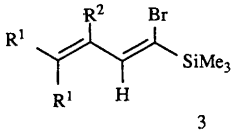

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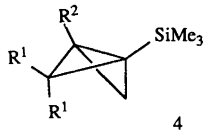
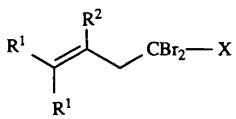


4

a, $R^1 = R^2 = H$
b, $R^1 = Me$, $R^2 = H$
c, $R^1 = H$, $R^2 = Me$



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Treatment of the silane **2a** with methyllithium at 25 °C in ether led to the bicyclo[1.1.0]butane **4a** (47 %), together with two minor products which were provisionally characterised as 1-bromo-1-trimethylsilylbut-3-ene and 1-bromo-1-trimethylsilylbuta-1,3-diene. The silane **4a** gave $^1$H NMR and IR data which were identical with those reported for this compound, obtained by trapping 1-lithiobicyclo[1.1.0]butane with trimethylsilyl chloride.[4] In the same way **2c** was converted into **4c**, and **2b** gave **4b** (53 %), which showed $\delta_H$ 0.0 (9 H, s), 0.96 (3 H, s), 1.2 (3 H, s), 1.16–1.46 (2 H, m) and 1.65 (1 H, d, $J$ = 2 Hz), together with minor less volatile products. The bicyclobutanes are apparently derived by intramolecular addition of an intermediate carbene (**7**) or a related carbenoid to the alkene double bond (Scheme 1).

Interestingly, the intermediate carbenes do not appear to undergo a 1,2-hydrogen shift, a reaction which is normally favoured in alkylcarbenes.[5] α-Phenyl-α-trimethylsilylcarbene and trimethylsilylcarbene itself have been obtained by photolysis of the corresponding diazo-compound and found to rearrange either through a 1,2-shift to produce a silene or to produce a silaindene.[6] They have also been obtained by pyrolysis of the organomercury **8**[7] and by pyrolysis of

† A preliminary account of some of this work has already appeared.[1]

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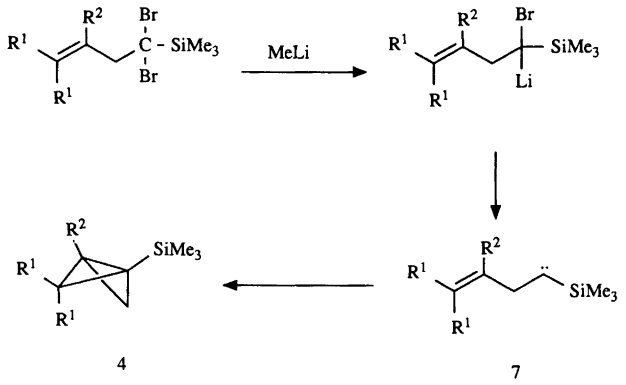
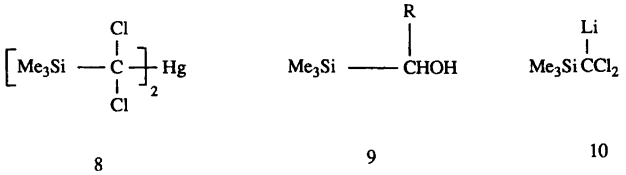


*Scheme 1.*

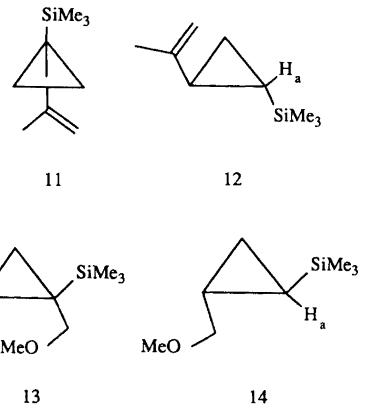
trimethylsilylalkanols **3** at 500 °C.[8] a-Elimination has been less successful, although the parent α-trimethylsilylcarbene has been obtained in low yield by this method.[9,10] The lithioalkanes **10** apparently decompose thermally by routes not involving carbenes.[11]



Bicyclo[1.1.0]butanes are known to undergo a variety of ring-opening reactions on treatment with acid or a metal catalyst.[12] In view of the known effect of silicon in stabilizing positive charge at the β- but not at the α-position,[13] it was of interest to examine the ring-opening of bicyclo[1.1.0]butanes **4**.

Reaction of **4b** with silver perchlorate in benzene for 18 h at 20 °C led to 1-isopropenyl-1-trimethylsilylcyclopropane (**11**) (57 %); 1,2,2-trimethylbicyclo[1.1.0]butane is reported to give 1-methyl-1-isopropenylcyclopropane together with butadienes on reaction with silver ion,[14] though the cyclopropane is the only product when the bicyclobutane is treated with acid.[15] The silyl group appears to moderate the reaction of **4b**, but the regiochemistry is as expected for the β-stabilizing effect of silicon. In contrast, the reaction of **4b** with catalytic toluene-*p*-sulphonic acid in benzene for 30 min at 20 °C led to *trans*-2-isopropenyl-1-trimethylsilylcyclopropane (**12**), the $^1$H NMR spectrum of which included a double triplet ($J$ = 10, 7 Hz) at δ −0.3 for $H_a$, including just one *cis*-coupling. The reason for this regiochemistry is not clear.

The corresponding parent compound (**4a**) did not react with either of the above reagents but, on treatment with silver perchlorate in methanol, was converted into a 1:1 mixture of the ethers **13** and **14**, which were separated by preparative GLC. The stereochemistry of the latter was assigned as *trans*- on the basis of the signal for $H_a$ which appeared as a double double doublet including one *cis*- (10 Hz) and two *trans*- (6.5 and 7.5 Hz) coupling constants. Repeating the reaction with silver perchlorate in $CH_3OD$ led to essentially complete loss of this signal. In the same way treatment of **4c** with silver perchlorate in methanol led to 1-methoxy-1-methyl-3-trimethylsilylcyclobutane, provisionally characterised as the isomer with methyl and trimethylsilyl groups *cis*-related. Once again, neither of these reactions appears to show a strong effect of silicon in stabilizing a β-cation.

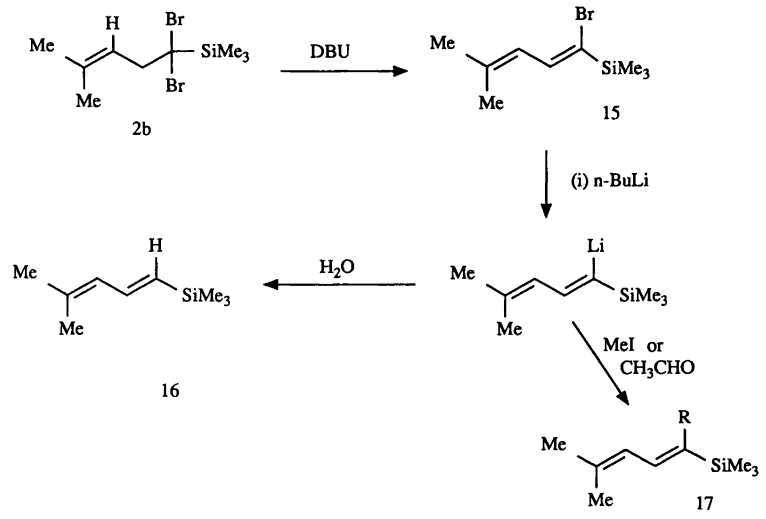


Treatment of the dibromide **2b** with diazabicycloundecene (DBU) in dichloromethane at 25 °C gave the diene **15** (70 %) (Scheme 2). The preparation of (*Z*)-1-bromo-1-trimethylsilylpenta-1,3-diene in two steps from crotonaldehyde has been reported;[16] lithium–bromine exchange and alkylation at C-1 then leads to a valuable synthetic intermediate. The formation of dienes such as **15** from the readily available tribromides (**1**) may provide a useful alternative. Treatment of **15** with *t*-butyllithium in tetrahydrofuran at −70 to −75 °C, followed by quenching with water gave the *E*-diene **16**.[17]

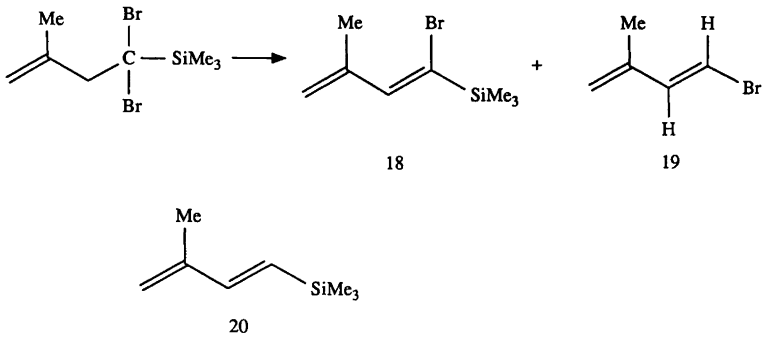
Quenching with $D_2O$ led to only partial incorporation of deuterium at C-1. However, treatment of **15** with *n*-butyllithium followed by quenching with $D_2O$ did lead to efficient incorporation of deuterium. It is not clear whether the proton source in the reaction with the former alkyllithium is an alkyl group originating in the reagent; protonation of organolithium species by reagents or solvent has been observed before.[18] In the same way, quenching of the lithiated diene with methyl iodide provided access to **17**, R = $CH_3$, while quenching with ethanal gave **17**, R = CH(OH)Me.

Treatment of the silane **2c** with DBU followed a different course. The minor product, (*Z*)-1-bromo-3-methyl-1-trimethylsilylbuta-1,3-diene (**18**) (34 %) was analogous to **15**, but the major product was (*E*)-1-bromo-3-methylbuta-1,3-diene (**19**) (54 %, Scheme 3). The latter was identical with the product of reaction of the dibromide (**5c**, X = H) with DBU in dichloromethane, and to the product of ring opening of 3-bromo-1-methylcyclobutene.[19]

Compound **18** underwent lithium–bromine exchange on reaction with butyllithium at −70 °C as above; quenching




*Scheme 2.*




*Scheme 3.*

with water led to *trans*-1-trimethylsilyl-3-methylbuta-1,3-diene (66%),[20] which was readily trapped by Diels–Alder addition to tetracyanoethene. The corresponding reaction of **2c** with DBU led to a 3.5:1 mixture of (*Z*)- and (*E*)-1-bromo-1-trimethylsilylbuta-1,3-dienes (51%) which could not be separated by column chromatography.

The above reactions provide an alternative route to synthetically valuable[21] 1-trimethylsilylbuta-1,3-dienes.

## Experimental

Organic solutions were dried over anhydrous sodium or magnesium sulfate. TLC was performed on Schleicher and Schull F15054 silica gel plates. Column chromatography was performed using Merck 7736 silica gel under low pressure. GLC was conducted using a Packard 427 gas chromatograph with a quartz SE30 capillary column or, for preparative work, a Varian Aerograph 2700 gas chromatograph with a 2 M 10% SE30 on Celite 60-85 column. Unless otherwise stated, all new compounds were pure by TLC or GLC. Melting points were determined on a Kofler hot-stage apparatus. Elemental analyses were performed with a Carlo-Erba Instrumentazione model 1106 CHN analyser. IR spectra were recorded on a Nicolet 20 SX B FT spectrometer. NMR spectra were recorded for deuteriochloroform solutions with tetramethylsilane as the internal standard unless otherwise stated. $^1$H NMR spectra were recorded on a Hitachi Perkin Elmer R24B at 60 MHz, or a Bruker WM 300-WB at 300 MHz, and $^{13}$C NMR spectra on the WM300-WB at 75 MHz. EI mass spectra were recorded on AEI MS 9; Br and Cl refer to the isotopes $^{79}$Br and $^{35}$Cl.

*Reaction of 1,1,1-tribromobut-3-ene with butyllithium and trimethylsilyl chloride.* The tribromide **1a** (7.0 g, 0.024 mol) in tetrahydrofuran (60 ml), ether (40 ml) and pentane (30 ml) was cooled to −120 °C. Butyllithium (20 ml of a 1.55 molar solution in hexane) was added at such a rate that the temperature did not exceed −115 °C throughout the addition. The solution was stirred at this temperature for a further 30 min before being quenched with trimethylsilyl chloride (10 ml, large excess). After the reaction mixture had warmed to 25 °C, it was poured into water (100 ml) and extracted with ether (100 ml). The organic layer was dried ($MgSO_4$) and evaporated at 14 mmHg. Distillation of the crude product at 0.05 mmHg gave a distillate (b.p. 35–40 °C) which was characterised as *1,1-dibromo-1-trimethylsilylbut-3-ene* (**2a**) (4.8 g, 69%) (Found: $M^+$ 283.9221, $C_7H_{14}Br_2Si$ requires $M$ 283.9232), which showed NMR: $\delta_H$

($CDCl_3$) 6.45–5.75 (1 H, m), 5.28 (1 H, d, $J = 10$ Hz), 5.21 (1 H, d, $J = 17$ Hz), 3.13 (2 H, d, $J = 7$ Hz), 0.3 (9 H, s); IR: $\nu_{max}$ (film) 845, 875, 1255, 1640 $cm^{-1}$; MS: *m/z* 288, 286, 284, 137, 132, 73.

*Reaction of the tribromide* **1c** *with butyllithium and trimethylsilyl chloride.* To a solution of the tribromide **1c** (1 g, 0.003 mol) in THF (8 ml), ether (5 ml) and pentane (4 ml) at −115 °C, butyllithium (1.2 molar equivalent) was added dropwise over 10 min. Trimethylsilyl chloride (0.7 g, 0.0066 mol) was added, maintaining the temperature −115 °C. After being stirred for 20 min, the mixture was allowed to warm to 20 °C and then extracted with ether. Evaporation of the dried ($MgSO_4$) organic layer afforded after purification (distillation, b.p. 60–65 °C/0.1 mmHg) *1,1-dibromo-3-methyl-1-trimethylsilylbut-3-ene* (**2c**) (50 %) (Found: $M^+$ 297.9366, $C_8H_{10}Br_2Si$ requires $M$ 297.9388), NMR: $\delta_H$ ($CCl_4$): 0.33 (9 H, s, $SiMe_3$), 2.06 (3 H, s, CMe), 3.06 (2 H, s, $CH_2CBr_2$), 4.93 (1 H, br s, $CH_2$:C) and 5.06 (1 H, br s, $CH_2$:C); IR: $\nu_{max}$ (film) 1255 (C−Si), 1645 (−C=C−) and 3090 $cm^{-1}$ (C−H); MS: *m/z* (*inter alia*) 298, 300, 302 (1:2:1) ($M^+$); 219, 221 (1:1) ($M^+$−Br) and 146, 148 (1:1) ($M^+$−Br, $SiMe_3$).

*Reaction of the tribromide* **1b** *with butyllithium and trimethylsilyl chloride.* To a cooled solution (−115 °C) of the tribromide **1b** (6.36 g, 0.02 mol) in THF (50 ml), ether (32 ml) and pentane (25 ml), butyllithium (1.2 molar equivalent) was added dropwise over 30 min. Trimethylsilyl chloride (4.3 g, 0.04 mol) was added to the yellow reaction mixture which was then allowed to warm to 20 °C, and extracted with ether. Evaporation of the washed ($H_2O$) and dried ($MgSO_4$) organic layer at 14 mmHg and column chromatography over silica eluting with light petroleum and ether gave a single product *1,1-dibromo-4-methyl-1-trimethylsilylpent-3-ene* (**2b**) (64 %), b.p. 72–76 °C/0.05 mmHg (Found: $M^+$ 311.9549, $C_9H_{18}Br_2Si$ requires $M$ 311.9544), NMR: $\delta_H$ ($CCl_4$) 0.36 (9 H, s, $SiMe_3$), 1.8 (3 H, s, CMe), 1.93 (3 H, s, CMe), 3.16 (2 H, d, $J = 7$ Hz, $CH_2CBr_2$) and 5.51 (1 H, br t, $J = 7$ Hz, C:CH); IR: $\nu_{max}$ (film) 1255 (C−Si), 1670 (C=C), 2920 and 2960 $cm^{-1}$ (C−H); MS: *m/z* (*inter alia*) 312, 314, 316 (1:2:1) ($M^+$); 160, 162 (1:1) ($M^+$−Br, SiMe) and 81 ($C_6H_9^+$, base peak).

*Reaction of 1,1,1-tribromo-4-methylpent-3-ene with butyllithium and water.* Compound **1b** (2.0 g, 6 mmol) was dissolved in dry tetrahydrofuran (15 ml), ether (10 ml) and pentane (7.5 ml) and the solution cooled to −120 °C. Butyllithium (5 ml of a 1.55 molar solution in hexane) was added dropwise with stirring at such a rate that the temperature remained between −115 and −120 °C throughout the addition. After 20 min of stirring at this temperature, water (10 ml) was added rapidly and the reaction allowed to warm to room temperature, when it was poured into water (50 ml) and extracted twice with ether (2 × 50 ml). The combined ethereal extracts were dried ($MgSO_4$), and the solvents removed at 14 mmHg to give a yellow oil which showed one major peak on GLC. Bulb-to-bulb distillation (furnace temperature 55–65 °C, 2 mmHg) gave a distillate which was characterised as *1,1-dibromo-4-methylpent-3-ene* (**5b**, X = H) (0.87 g, 58 %) (Found: $M^+$ 239.9172, $C_6H_{10}Br_2$ requires $M$ 239.9149), and showed NMR: $\delta_H$ ($CDCl_3$) 1.66 (3 H, s), 1.75 (3 H, s), 3.12 (2 H, t, $J = 7$ Hz), 5.23 (1 H, t, $J = 7$ Hz), 5.73 (1 H, t, $J = 7$ Hz); IR: $\nu_{max}$ (film) 2940, 1445, 835, 670 $cm^{-1}$.

*Reaction of 1,1,1-tribromo-4-methylpent-3-ene with butyllithium and ethyl acetate.* Compound **1b** (2.0 g, 6 mmol) was dissolved in dry tetrahydrofuran (15 ml), ether (10 ml) and pentane (7.5 ml) and the solution cooled to −120 °C. Butyllithium (5.5 ml of a 1.55 molar solution in hexane) was added dropwise with stirring at such a rate that the temperature remained between −115 °C and −120 °C throughout the addition. The reaction mixture was stirred at this temperature for 20 min, and then ethyl acetate (5 ml) was added over approximately 5 min. The reaction was then allowed to warm to −100 °C and sulphuric acid (20 ml of a 2 molar solution) was added rapidly. The reaction mixture was allowed to reach room temperature, when it was poured into water (50 ml) extracted twice with ether (2 × 50 ml) and the combined ethereal extracts dried ($MgSO_4$). The solvents were removed at 14 mmHg and any volatile impurities (mainly bromobutane and residual solvents) were distilled off at 0.1 mmHg. The residue, which showed one major spot by TLC, was purified by column chromatography over silica, eluting with light petroleum (b.p. 40–60 °C), to give a colourless oil, which was characterised as *3,3-dibromo-6-methylhept-5-en-2-one* (**5b**, X=COMe) (1.1 g, 63 %) (Found: $M^+$ 281.9290, $C_8H_{12}Br_2O$ requires $M$ 281.9255) which showed NMR: $\delta_H$ ($CDCl_3$) 1.66(3H,s),1.76(3H,s),2.66(3H,s),3.15(2 H,d,$J = 7$Hz), 5.2 (1 H, t, $J = 7$ Hz); IR: $\nu_{max}$ (film) 2860, 1735, 1445 $cm^{-1}$.

*Reaction of 1,1,1-tribromo-4-methylpent-3-ene with butyllithium and allyl bromide.* Compound **1b** (6.0 g, 18.7 mmol) in dry tetrahydrofuran (45 ml), ether (30 ml) and pentane (22.5 ml) was cooled to −120 °C. Butyllithium (16 ml of a 1.55 molar solution in hexane), was added dropwise, with stirring, at such a rate that the temperature did not exceed −115 °C throughout the addition. The solution was stirred at this temperature and after 20 min allyl bromide (5 ml) was added dropwise over approximately 5 min. The reaction mixture was allowed to reach 25 °C and after extraction between water and ether and evaporation of the dried organic extracts at 14 mmHg, an oil was obtained which showed one major peak by GLC. Distillation at 0.05 mmHg and 59–60 °C gave a product which was characterised as *4,4-dibromo-6-methylocta-1,7-diene* (**5b**, X = allyl) (2.4 g, 46 %) (Found: $M^+$ 279.9464, $C_9H_{14}Br_2$ requires $M$ 279.9462) which showed NMR: $\delta_H$ ($CDCl_3$) 5.0–5.9 (5 H, m), 3.15 (4 H, br d, $J$ = ca. 7 Hz), 1.75 (3 H, s), 1.65 (3 H, s); IR: $\nu_{max}$ (film) 2880, 1440, 790 $cm^{-1}$.

*Reaction of 1,1-dibromo-1-trimethylsilylbut-3-ene with methyllithium.* The dibromide **1a** (1 g, 3.5 mmol) in ether (30 ml) was stirred at 25 °C. Methyllithium (15 ml of a 0.7 molar solution in ether) was added over 10 min and the reaction allowed to stir at 25 °C for 30 min. Excess lithium reagent was quenched with water (20 ml) and the aqueous layer extracted with ether (20 ml). The combined ethereal extracts were dried ($MgSO_4$) and most of the ether distilled at 760 mmHg. The residue was flash distilled at 14 mmHg to give 1-trimethylsilylbicyclo[1.1.0]butane (**4a**) (distilled yield 47 %), identified by comparison of its NMR and infrared data with those reported for an authentic sample.[3]

The residue then showed one major peak by GLC which after collection was identified as an impure sample of *1-bromo-1-trimethylsilylbut-3-ene* (ca. 20 %), which showed NMR: $\delta_H$ ($CDCl_3$) 6.05–5.4 (1 H, m), 5.07 (2 H, m), 3.33 (1 H, dd, $J = 9$, 5 Hz), 2.55 (2 H, m), 0.2 (9 H, s); IR: $\nu_{max}$ (film) 940, 1255, 1640 $cm^{-1}$; MS: *m/z* 206, 191, 127 ($M^+$ too small for mass measurement). Also present: *m/z* 204 (Found $M^+$ 203.9953, $C_7H_{13}BrSi$ requires *M* 203.9970), 189, 125, 73, attributed to a trace of *1-bromo-1-trimethylsilylbuta-1,3-diene.* Reinjection of the sample into the GLC failed to separate the components.

*Reaction of 1,1-dibromo-3-methyl-1-trimethylsilylbut-3-ene with methyllithium.* The dibromide **2c** (400 mg, 1.34 mmol) in dry ether (10 ml) was stirred at 25 °C. Methyllithium (2.7 ml of a 1.5 molar solution in ether) was added dropwise over 10 min and after a further 10 min the reaction was quenched with water (10 ml). The two layers were separated and the ethereal layer was washed with water. The combined aqueous washings were extracted with ether (10 ml) and the combined ethereal extracts were dried ($MgSO_4$). Most of the ether was distilled at 760 mmHg, and the residue was flash distilled at 14 mmHg. GLC examination of the distillate and the residue indicated one major volatile and a minor involatile product, respectively. The distillate contained only ether and the volatile component which was collected and identified as *1-methyl-3-trimethylsilylbicyclo[1.1.0]butane* (**4c**) (distilled yield 48 %) (Found: $M^+$ 126.0871, $C_7H_{14}Si$ requires *M* 126.0865) which showed NMR: $\delta_H$ ($CDCl_3$) 1.58 (3 H, s), 1.15 (2 H, s), 0.3 (2 H, s), 0.05 (9 H, s); IR: $\nu_{max}$ (ether) 2848, 1250, 840 $cm^{-1}$.

The residue was also subjected to preparative GLC. From its NMR it could be seen that more than one component was present, the major compound being tentatively identified as 1-bromo-3-methyl-1-trimethylsilylbut-3-ene (ca. 22 %), which showed NMR: $\delta_H$ ($CDCl_3$) 0.1 (9 H, s), 1.73 (3 H, br s), 2.53 (2 H, m), 3.35 (1 H, dd, $J = 10$, 5 Hz), 4.8 (2 H, m); IR: $\nu_{max}$ (film) 2960, 1252, 840 $cm^{-1}$. Reinjection of the collected sample into the GLC showed little separation of the components.

*Reaction of the dibromosilane* **2b** *with methyllithium.* Methyllithium (1.5 molar equivalent) was added to a solution of the dibromide **2b** (1.8 g, 0.0057 mol) in dry ether (15 ml) at 20 °C. After 10 min the reaction mixture was quenched with water (2 ml) and diluted with ether. Evaporation of the dried ($MgSO_4$) organic layer at 34 °C/760 mmHg afforded a single product, *2,2-dimethyl-1-trimethylsilylbicyclo[1.1.0]butane* (**4b**) (53 %) which was purified by distillation (b.p. 60 °C/14 mmHg) (Found: $M^+$ 154.1183, $C_9H_{18}Si$ requires *M* 154.1178), NMR: $\delta_H$ ($CCl_4$) 0 (9 H, s, $SiMe_3$), 0.96 (3 H, s, CMe), 1.2 (3 H, s, CMe), 1.16–1.46 (2 H, m, bicyclobutane $CH_2$), 1.65 (1 H, d, $J = 2$ Hz, bicyclobutane CH); IR: $\nu_{max}$ (film) 845 (C–H), 1254 (C–Si), 2960 $cm^{-1}$ (C–H).

*Reaction of the bicyclobutane* **4b** *with silver perchlorate in benzene.* Silver perchlorate (0.05 g, 0.0002 mol) was added to a solution of the bicyclobutane **4b** (0.025 g, 0.00015 mol) in benzene (1 ml). After 18 h at 20 °C, filtration, followed by evaporation of the organic phase at 42 °C/760 mmHg afforded *1-isopropenyl-1-trimethylsilylcyclopropane* (**11**) (42 %) which was purified by preparative GLC (Found: $M^+$ 154.1181, $C_9H_{18}Si$ requires *M* 154.1178), NMR: $\delta_H$ ($CCl_4$) 0.21 (9 H, s, $SiMe_3$), 0.78 (4 H, s, cyclopropane $CH_2$), 2.0 (3 H, s, CMe) and 5.06 (2 H, br s, $CH_2$:C); IR: $\nu_{max}$ (film) 840 (C–H), 1255 (Si–C) and 3080 $cm^{-1}$ (C–H); MS: *m/z* (*inter alia*) 154 ($M^+$), 139 ($M^+ - CH_3$), 113 ($M^+ - C_3H_5$) and 73 ($C_3H_9Si^+$, base peak).

*Reaction of the bicyclobutane* **4b** *with toluene-*p*-sulphonic acid.* Toluene-*p*-sulphonic acid (0.02 g, 0.001 mol) was added to a solution of the bicyclobutane **4b** (0.25 g, 0.0016 mol) in benzene (5 ml). After 0.5 h at 20 °C, the reaction mixture was diluted with dichloromethane and washed with saturated aq. sodium hydrogencarbonate followed by water. Evaporation of the dried ($MgSO_4$) organic layer at 42 °C/760 mmHg left an oil (0.11 g) which on purification by preparative GLC afforded *1-isopropenyl-2-trimethylsilylcyclopropane* (**12**) (45 %) (Found: $M^+$ 154.1183, $C_9H_{18}Si$ requires *M* 154.1178), NMR: $\delta_H$ ($CCl_4$) −0.15–0 (1 H, ddd, $J = 10$, 7, 7 Hz, cyclopropane $CH_2$), 0.156 (9 H, s, $SiMe_3$), 0.67–0.79 (1 H, ddd, $J = 7$, 7, 4 Hz, $CHSiMe_3$), 0.93–1.05 (1 H, ddd, $J = 10$, 4, 4 Hz, cyclopropane $CH_2$), 1.51–1.64 (1 H, ddd, 7, 7, 4 Hz, CHC), 1.82 (3 H, s, CMe), 4.84 (1 H, s, $CH_2$) and 4.92 (1 H, s, $CH_2$); IR: $\nu_{max}$ (film) 840 (C–H), 1250 (C–Si) and 3080 $cm^{-1}$ (C–H).

*Reaction of 1-trimethylsilylbicyclo[1.1.0]butane with silver perchlorate and methanol.* (a) To a solution of **4a** (67 mg, 0.53 mmol) in ether (1 ml) and methanol (0.5 ml) was added silver perchlorate (approximately 10 mg). A yellow precipitate was immediately formed and after 10 min the filtered solution showed two peaks by GLC, ratio 1:1. The solvents were distilled off at 14 mmHg and the residue was purified by preparative GLC and the two products were characterised as trans-*1-(methoxymethyl)-2-trimethylsilylcyclopropane* (**14**) (17 mg, 25 %) (Found: $M^+$ 158.1116, $C_8H_{18}OSi$ requires *M* 158.1127) which showed NMR: $\delta_H$ ($CDCl_3$) 3.53 (3 H, s), 3.52 (1 H, dd, $J = 9.5$, 5 Hz), 3.36 (1 H, dd, $J = 9.5$, 7 Hz), 1.17 (1 H, dtt, $J = 6$, 7 Hz),

0.6–0.7 (2 H, m), 0.05 (9 H, s), −0.3 (1 H, ddd, $J = 10, 7.5, 6.5$ Hz); IR: $\nu_{max}$ (film) 840, 1120, 1250 $cm^{-1}$; *m/z* 143, 115, 89, 73 and *1-methoxymethyl-1-trimethylsilylcyclopropane* (**13**) (25%, GLC estimation) which showed NMR: $\delta_H$ ($CDCl_3$) 3.32 (3 H, s), 3.2 (2 H, s), 0.48 (4 H, m), 0.01 (9 H, s); IR: $\nu_{max}$ (film) 840, 1110, 1250, 2960, 3070 $cm^{-1}$; MS: *m/z* 158 (too small for mass measurement), 143, 115, 89, 73.

(b) The reaction was performed as in (a) but using $CH_3OD$. One of the products was isolated by preparative GLC and identified as cis-*1-deuterio*-cis-*2-methoxy*-trans-*1-trimethylsilylcyclopropane,* which showed NMR: $\delta_H$ ($CDCl_3$) 3.53 (3 H, s), 3.52 (1 H, dd, $J = 9.5$, 6 Hz), 3.36 (1 H, dd, $J = 9.5$, 7 Hz), 1.17 (1 H, br quintet, $J =$ ca. 6.5 Hz), 0.7–0.6 (2 H, m), 0.01 (9 H, s).

*Reaction of 1-methyl-3-trimethylsilylbicyclo[1.1.0]butane with silver perchlorate and methanol.* To a solution of **4c** (31 mg, 0.22 mmol) in ether (0.5 ml) was added methanol (0.3 ml) and silver perchlorate (10 mg). After being allowed to stand at 25 °C for 10 min, the filtered solution showed one major peak by GLC. The ether and some of the methanol was flash distilled off at 14 mmHg along with a small amount of the product. The residue was purified by preparative GLC and the product isolated was characterised as *1-methoxy-1-methyl-3-trimethylsilylcyclobutane* (12 mg, 40%) (Found: $M^+$ 172.1281, $C_9H_{20}SiO$ requires *M* 172.1283) which showed NMR: $\delta_H$ ($CDCl_3$, 360 MHz) −0.5 (9 H, s), 1.19 (3 H, s), 1.66 (1 H, m, including two couplings of 9.5 Hz and two of 10.5 Hz), 1.77 (4 H, m), 3.19 (3 H, s); IR: $\nu_{max}$ (film) 2960, 1250, 1080, 840 $cm^{-1}$.

*Reaction of the dibromide* **2a** *with 1,8-diazabicyclo[5.4.0]-undec-7-ene.* 1,8-Diazabicyclo[5.4.0]undec-7-ene (3 g, 0.019 mol) was added dropwise to a solution of the dibromide **2a** (5 g, 0.017 mol) in $CH_2Cl_2$ (50 ml) at 20 °C. After 24 h, the solvent was evaporated off at 42 °C/760 mmHg to leave a residual oil (2.0 g). Bulb-to-bulb distillation (oven temperature 50–60 °C/2 mmHg) gave a mixture of two products (3.5:1) which could not be separated by preparative GLC or silica-gel chromatography. Spectroscopic evidence suggested the two products to be *cis-* and *trans*-1-bromo-1-trimethylsilylbuta-1,3-diene (overall yield 51%) (Found: $M^+$ 203.9988, $C_7H_{13}BrSi$ requires *M* 203.9970), NMR: $\delta_H$ ($CCl_4$) 0–0.5 (18 H, two singlets, $SiMe_3$), 5.0–5.53 (4 H, m, C=CH−CH=C), 6.33–6.86 (4 H, m, $CH_2$=CH); IR: $\nu_{max}$ (film) 760 (C−Br), 1253 (C−Si), 1680 (−C=C−) and 2960 $cm^{-1}$ (C−H); MS: *m/z* (*inter alia*) 204, 206 (1:1) ($M^+$); 189, 191 (1:1) ($M^+-CH_3$) and 131, 133 (1:1) ($M^+-SiMe_3$).

*Reaction of 1,1-dibromo-4-methyl-1-trimethylsilylpent-3-ene with diazabicyclo[5.4.0]undec-7-ene.* Compound **2b** (4.7 g, 0.012 mmol) and dichloromethane (50 ml), were stirred at 25 °C. Diazabicycloundecene (2.7 g, 0.018 mol) was added dropwise over 5 min, and the reaction mixture was stirred for 18 h. Excess base was neutralised with hydrochloric acid (50 ml of a 2 molar solution) and the aqueous washings were extracted with dichloromethane (50 ml). The combined organic extracts were dried ($MgSO_4$) and the solvent was removed at 14 mmHg. Column chromatography of the resulting oil over silica, eluting with light petroleum and ether, gave a product that was identified as *1-bromo-4-methyl-1-trimethylsilylpenta-1,3-diene* (**15**) (2.5 g, 70%) (Found: $M^+$ 232.0294, $C_9H_{17}SiBr$ requires *M* 232.0283) which showed NMR: $\delta_H$ ($CDCl_3$) 0.16 (9 H, s), 1.81 (6 H, br s), 5.87 (2 H, ABdd, $J = 10$ Hz); IR: $\nu_{max}$ (film) 840, 1250, 1640, 2940 $cm^{-1}$.

*Reaction of 1-bromo-4-methyl-1-trimethylsilylpenta-1,3-diene with* tert*-butyllithium and water.* Compound **15** (865 mg, 5 mmol) in tetrahydrofuran (10 ml) was cooled to −70 °C. *tert*-Butyllithium (6.5 ml of a 1.5 molar solution in hexane) was added dropwise over 10 min and the reaction was stirred at −70 °C for 2 h. Water (10 ml) was added and the reaction allowed to warm to 25 °C. After extraction with ether (100 ml) and washing with water (100 ml), the organic extract was dried ($MgSO_4$) and evaporated at 14 mmHg. Column chromatography of the crude product over silica, eluting with petroleum, afforded a colourless oil which was further purified by preparative GLC. The product was characterised as *(E)-4-methyl-1-trimethylsilylpenta-1,3-diene* (**16**) (316 mg, 55%) (Found: $M^+$ 153.1190, $C_9H_{18}Si$ requires *M* 154.1178), which showed NMR: $\delta_H$ ($CDCl_3$) 6.8 (1 H, dd, $J = 18$, 10 Hz), 5.95 (1 H, br d, $J = 10$ Hz), 5.73 (1 H, d, $J = 18$ Hz), 1.95 (6 H, br s), 0.23 (9 H, s); IR: $\nu_{max}$ (film) 835, 870, 1250, 1645, 2960 $cm^{-1}$.

*Reaction of 1-bromo-4-methyl-1-trimethylsilylpenta-1,3-diene with butyllithium and deuterium oxide.* (a) Compound **15** (400 mg, 1.72 mmol) in tetrahydrofuran (10 ml) was cooled to −70 °C. *tert*-Butyllithium (3.5 ml of a 1.5 molar solution in hexane) was added dropwise over approximately 5 min and the reaction was allowed to stir at −70 °C, for a further 2 h. After this time deuterium oxide (2 ml) was added and the mixture allowed to warm to 25 °C. After extraction with ether (40 ml), and washing with water (25 ml), the organic extract was dried ($MgSO_4$) and evaporated at 14 mmHg. The crude product was subjected to preparative GLC and the NMR spectrum of the sample collected was identical with that for **16**. The mass spectrum showed a molecular ion at *m/z* 154, and no evidence of any deuteriated product.

(b) The reaction was carried out as in (a) except that the deuterium oxide was added after 10 min at −70 °C. After work-up as above, the oil obtained gave a complex NMR spectrum that included signals due to **16**. The mass spectrum showed two peaks of approximately equal height at *m/z* 154 and 155, indicating ca. 50% deuterium incorporation.

(c) Compound **15** (400 mg, 1.72 mmol) in dry tetrahydrofuran (10 ml) was cooled to −70 °C. Butyllithium (4.3 ml of a 15% w/w solution in hexane) was added at

such a rate that the temperature did not exceed −60 °C. The reaction was stirred at this temperature for a further 10 min, when deuterium oxide (3 ml) was added and the reaction mixture allowed to warm to room temperature. The resulting suspension was poured into water (50 ml), extracted twice with ether (2 × 25 ml) and the combined ethereal extracts dried ($MgSO_4$). The solvents were removed at 14 mmHg to furnish a yellow oil which, after column chromatography over silica, eluting with light petroleum, was further purified by preparative GLC. The product was characterised as *1-deuterio-4-methyl-1-trimethylsilylpenta-1,3-diene* (111 mg, 41 %) (Found: $M^+$ 155.1254, $C_9H_{17}DSi$ requires $M$ 155.1240), which showed NMR: $\delta_H$ ($CDCl_3$) 0.1 (9 H, s), 1.82 (1 H, br s), 6.3 (2 H, ABdd, $J = 11$ Hz).

*Reaction of 1-bromo-4-methyl-1-trimethylsilylpenta-1,3-diene with butyllithium and methyl iodide.* Compound **15** (300 mg, 1.3 mmol) in dry tetrahydrofuran (10 ml) was cooled to −70 °C. Butyllithium (3 ml of a 15 % w/w solution in hexane) was added at such a rate that the temperature did not exceed −60 °C and the solution was allowed to stir at this temperature for 10 min. Excess methyl iodide (1 ml, 2.28 g) was added rapidly and the reaction mixture was allowed to warm to room temperature, poured into water (50 ml) and extracted with ether (50 ml). The ethereal extract was dried ($MgSO_4$) and the solvents removed at 14 mmHg, to give an oil, which after column chromatography was further purified by preparative GLC. The product was characterised as *5-methyl-2-trimethylsilylhexa-2,4-diene* (**17**, R = Me) (200 mg, 69 %) (Found: $M^+$ 168.1340, $C_{10}H_{20}Si$ requires $M$ 168.1344), which showed NMR: $\delta_H$ ($CDCl_3$) 0.1 (9 H, s), 1.73 (9 H, br s), 6.38 (2 H, ABdd, $J = 10$ Hz); IR: $\nu_{max}$ (film) 830, 850, 1245, 1640 $cm^{-1}$.

*Reaction of 1-bromo-4-methyl-1-trimethylsilylpenta-1,3-diene with butyllithium and acetaldehyde.* Compound **3b** (0.4 g, 1.8 mmol) in dry tetrahydrofuran (10 ml) was cooled to −70 °C. Butyllithium (3 ml of a 15 % w/w solution in hexane) was added at such a rate that the temperature did not exceed −65 °C and the solution was stirred at this temperature for 15 min. Excess acetaldehyde (1 ml, 0.8 g) was added rapidly, and the reaction mixture allowed to warm to room temperature, poured into water (50 ml) and extracted with ether (50 ml). The ethereal extract was dried ($MgSO_4$) and removal of the solvents at 14 mmHg gave an oil whose TLC showed one major slow-running spot. Column chromatography of the oil over silica, eluting with dichloromethane, gave a product which was characterised as *6-methyl-3-trimethylsilylhepta-3,5-dien-2-ol* [**17**, R = CH(OH)Me] (181 mg, 53 %) (Found: $M^+$ 198.1449, $C_{11}H_{22}OSi$ requires $M$ 198.1440) which showed NMR: $\delta_H$ ($CDCl_3$) 0.15 (9 H, s), 1.3 (3 H, d, $J = 6$ Hz), 1.65 (1 H, br s, exchangeable with $D_2O$), 1.8 (6 H, s), 5.0 (1 H, q, $J = 6$ Hz), 6.3 (2 H, ABdd, $J = 11$ Hz); IR: $\nu_{max}$ (film) 3420, 2960, 1635, 1245, 835 $cm^{-1}$. A minor fast-running component was isolated and identified as *4-methyl-1-trimethylsilylpenta-1,4-diene* (48 mg).

*Reaction of 1,1-dibromo-3-methyl-1-trimethylsilylbut-3-ene with diazabicycloundecene.* Compound **2c** (6 g, 0.02 mol) was dissolved in dichloromethane (100 ml) and diazabicycloundecene (4 g, 0.026 mol) was added dropwise with stirring at 25 °C over approximately 10 min. The reaction was stirred at this temperature and was monitored by GLC noting the disappearance of the starting material and the appearance of a more volatile component. After 24 h, work-up as before and removal of most of the solvent at 760 mmHg gave a residue the NMR spectrum of which indicated two major components. These did not separate efficiently upon vacuum distillation. The more volatile product was identified as *1-bromo-3-methylbuta-1,3-diene* (**19**) (54 %, as estimated by NMR spectroscopy) by comparison of spectra with those from an independently synthesised sample (see below).

The second product was isolated by preparative GLC and characterised as *1-bromo-3-methyl-1-trimethylsilylbuta-1,3-diene* (**18**) (34 %) (Found: $M^+$ 218.0126, $C_8H_{15}BrSi$ requires $M$ 218.0126) which showed NMR: $\delta_H$ ($CDCl_3$) 0.25 (9 H, s), 2.09 (3 H, br s), 5.2 (2 H, m), 6.67 (1 H, s); IR: $\nu_{max}$ (film) 750, 1250, 1450 $cm^{-1}$.

*Reaction of 1-bromo-3-methyl-1-trimethylsilylbuta-1,3-diene with butyllithium and water.* Compound **18** (500 mg, 2.28 mmol) in dry tetrahydrofuran (10 ml) was cooled to −70 °C. Butyllithium (3 ml of a 1.65 molar solution in hexane) was added dropwise over approximately 5 min and the solution was stirred at −70 °C for 20 min. Water (10 ml) was added, and the reaction allowed to warm to 25 °C. The ether layer was separated and the aqueous layer extracted with ether (15 ml). The combined ethereal extracts were washed several times with water and dried ($MgSO_4$). Most of the solvent was removed by careful distillation at 14 mmHg and 0 °C. The residue was flash distilled at 0.01 mmHg and further purified by preparative GLC before being characterised as trans-*3-methyl-1-trimethylsilylbuta-1,3-diene* (210 mg, 66 %) (Found: $M^+$ 140.1014, $C_8H_{16}Si$ requires $M$ 140.1021) which showed NMR: $\delta_H$ ($CDCl_3$) 6.69 (1 H, d, $J = 19$ Hz), 5.86 (1 H, d, $J = 19$ Hz), 5.08 (2 H, br s), 2.91 (3 H, br s), 0.12 (9 H, s); IR: $\nu_{max}$ (film) 840, 870, 1250, 1580 $cm^{-1}$; MS: *m/z* 125, 99, 73.

*Reaction of 3-methyl-1-trimethylsilylbuta-1,3-diene with tetracyanoethylene.* The above diene (100 mg, 0.714 mmol) and tetracyanoethylene (95 mg, 0.742 mmol) were dissolved in $C_6D_6$ at 25 °C. The reaction was monitored by NMR spectroscopy and after 15 min, all of the signals due to the diene had disappeared. Unchanged tetracyanoethylene was filtered off and the deuteriobenzene removed at 14 mmHg. The crude product was recrystallised from aqueous ethanol and characterised as *5-methyl-3,3,4,4-tetracyano-2-trimethylsilylcyclohexene* (181 mg, 94 %, m.p.

95–96 °C) (Found: $M^+$ 268.1130, C, 62.90, H, 5.98, N, 20.66 %, $C_{14}H_{16}N_4Si$ requires C, 62.69, H, 5.97, N, 20.90 %, *M* 268.1144) which showed NMR: $\delta_H$ ($CDCl_3$) 5.6 (1 H, br s), 3.11 (2 H, br s), 2.69 (1 H, m), 2.0 (3 H, br s), 0.44 (9 H, s); IR: $\nu_{max}$ (KBr) 845, 1260, 2255 $cm^{-1}$.

*Reaction of 1,1,1-tribromo-3-methylbut-3-ene with butyllithium and water.* Compound **1c** (10 g, 0.033 mol) in dry tetrahydrofuran (75 ml), ether (50 ml) and pentane (38 ml) was cooled to −120 °C. Butyllithium (25 ml of a 1.6 molar solution in hexane) was added dropwise with stirring at such a rate that the temperature did not exceed −110 °C throughout the addition. The solution was stirred at this temperature for 15 min, when it was quenched rapidly with water (10 ml). After the reaction mixture had reached room temperature, it was poured into water (300 ml), extracted twice with ether (2 × 250 ml) and the ethereal extracts dried ($MgSO_4$). Removal of the solvents at 14 mmHg, gave an oil which showed two peaks by GLC. The first peak was collected and found to be *n*-butyl bromide. The second component was obtained by distillation, b.p. 60–64 °C at 14 mmHg and characterised as *1,1-dibromo-3-methylbut-3-ene* (**5c**, X = H) (4.0 g, 54 %) (Found: $M^+$ 225.8992, $C_5H_8Br_2$ requires *M* 225.8993) which showed NMR: $\delta_H$ ($CDCl_3$) 1.9 (3 H, s), 3.29 (2 H, d, $J$ = 7 Hz), 5.0 (1 H, br s), 5.1 (1 H, br s), 5.89 (1 H, t, $J$ = 7 Hz); IR: $\nu_{max}$ (film) 910, 1440, 2970 $cm^{-1}$.

*Reaction of 1,1-dibromo-3-methylbut-3-ene with diazabicycloundecene.* Compound **5c**, X = H (7.5 g, 0.033 mol) in dichloromethane (30 ml) was stirred at 25 °C. Diazabicycloundecene (5.5 g, 0.036 mol) was added dropwise over 2 min and the ensuing reaction was monitored by GLC. After 3 h, the reaction mixture was washed with dilute hydrochloric acid (50 ml of a 10 % aqueous solution) and the organic layer was dried ($MgSO_4$). Most of the solvent was distilled off at 760 mmHg to give a crude oil which showed one major peak by GLC. Flash distillation at 0.01 mmHg gave trans-*1-bromo-3-methylbuta-1,3-diene* (**19**) (3.9 g, 81 %) (Found: $M^+$ 145.9718, $C_5H_7Br$ requires *M* 145.9731) which showed NMR: $\delta_H$ ($CDCl_3$) 1.92 (3 H, br s), 5.12 (2 H, s), 6.67 (2 H, ABdd, $J$ = 14 Hz); IR: $\nu_{max}$ (film) 2970, 1450, 750 $cm^{-1}$; MS: *m/z* 131, 67.

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## References


1. Baird, M. S., Buxton, S. R. and Mitra, M. M. *Tetrahedron Lett.* (1982) 2701.
2. Baird, M. S., Baxter, A. G. W., Devlin, B. R. J. and Searle, R. J. G. *J. Chem. Soc., Chem. Commun.* (1979) 210; Labeish, N. N., Kharicheva, E. M., Mandelshtam, T. V. and Kostikov, R. R. *Zh. Org. Khim. 14* (1978) 878 (*Chem. Abstr. 89,* 23809x); Mandelshtam, T. V., Kharicheva, E. M., Labeish, N. N. and Kostikov, R. R., *Zh. Org. Khim. 16* (1980) 2513 (*Chem. Abstr. 94,* 120901b); Dehmlow, E. V. and Wilkenloh, J. *Tetrahedron Lett.* (1987) 5489.
3. Köbrich, G. and Werner, W. *Tetrahedron Lett.* (1969) 218; Villieras, J., Bacquet, C. and Normant, J. F. *Bull. Soc. Chim. France* (1975) 1797; *J. Organomet. Chem. 40* (1972) C1; *97* (1973) 325; Villieras, J., Rambaud, M., Tarhouni, R. and Kirschleger, B. *Synthesis* (1981) 68.
4. Cohen, H. M. *J. Organomet. Chem. 9* (1967) 357.
5. Kirmse, W. *Carbene Chemistry,* 2nd ed., Academic Press, NY; but-3-en-1-ylidene undergoes a 1,2-hydrogen shift in competition with cyclisation to bicyclo[1.1.0]butane (Lemal, D. M., Menger, F. and Clark, G. W. *J. Am. Chem. Soc. 85* (1963) 2529).
6. Ando, W., Sekiguchi, A., Hagiwara, T. and Migita, T. *J. Chem. Soc., Chem. Commun.* (1974) 372; Ando, W., Sekiguchi, A. and Migita, T. *J. Am. Chem. Soc. 97* (1975) 7159; Ando, W., Sekiguchi, A., Ogiwara, J. and Migita, T. *J. Chem. Soc., Chem. Commun.* (1975) 145; Chambers, G. and Jones, M. *Tetrahedron Lett.* (1978) 5193; Sekiguchi, A. and Ando, W. *J. Org. Chem. 45* (1980) 5286, *J. Am. Chem. Soc. 103* (1981) 3579; Haszeldine, R. N., Scott, D. L. and Tipping, A. E., *J. Chem. Soc., Perkin Trans. 1* (1974) 1440; Dow, A., Menzal, H. and Flood, T. C. *J. Am. Chem. Soc. 90* (1968) 1980; Kreeger, R. L. and Schecter, H. *Tetrahedron Lett.* (1975) 2061; Chapman, O. L., Chang, C. C., Kolc, M., Jung, M. E., Lowe, J. A., Barton, T. J. and Turvey, M. L. *J. Am. Chem. Soc. 98* (1976) 7844; Chedekel, M. R., Skoglund, M., Kreeger, R. L. and Schecter, H. *J. Am. Chem. Soc. 98* (1976) 7846; Ando, W. and Barton, T. J. *J. Am. Chem. Soc. 99* (1977) 6995; Sekiguchi, A., Ando, W. and Barton, T. J. *J. Org. Chem. 50* (1977) 3067; Barton, T. J., Kilgour, J. A., Gallucci, R. R., Rothschild, A. J., Slutsky, J., Wolf, A. D. and Jones, M. *J. Am. Chem. Soc. 97* (1975) 657.
7. Seyferth, D. and Hanson, E. M. *J. Organomet. Chem. 27* (1971) 19.
8. Sekiguchi, A. and Ando, W. *Tetrahedron Lett.* (1979) 4077.
9. Olofson, R. A., Hoskin, D. H. and Lotts, K. D. *Tetrahedron Lett.* (1978) 1677; Conolly, J. W. and Fryer, P. F. *J. Organomet. Chem. 30* (1971) 315.
10. Skell, P. S. and Goldstein, E. J. *J. Am. Chem. Soc. 86* (1964) 1442.
11. Cook, F. and Magnus, P. *J. Chem. Soc., Chem. Commun.* (1977) 513; Burford, C., Cook, F., Ehrlinger, E. and Magnus, P. *J. Am. Chem. Soc. 99* (1977) 4536; Barton, T. J. and Hoekman, S. K. *J. Am. Chem. Soc. 102* (1980) 1584; Seyferth, D., Hanson, E. M. and Armbrecht, F. M. *J. Organomet. Chem. 23* (1970) 361; Seyferth, D., Lambert, R. L. and Hanson, E. M. *J. Organomet. Chem. 24* (1970) 647.
12. See e.g., Closs, G. E. and Pfeffer, P. E. *J. Am. Chem. Soc. 90* (1968) 2452; Paquette, L. A. *Metal-catalysed Reactions in Strained Ring Compounds,* MPT International Review of Science, Organic Chemistry, Vol. 5. In: Parker, W., Ed., *Alicyclic Compounds,* Butterworths, 1973.
13. Colvin, E. *Silicon in Organic Synthesis,* Butterworths, 1981.
14. Paquette, L. A., Henzel, R. P. and Wilson, S. E. *J. Am. Chem. Soc. 94* (1972) 7780.
15. Skattebøl, L. *Acta Chem. Scand. 17* (1963) 1683; *Tetrahedron Lett.* (1970) 2361; Moore, W. R., Taylor, K. G., Müller, P., Hall, S. S. and Gaibel, Z. L. F. *Tetrahedron Lett.* (1970) 2365.
16. Wrobel, J. E. and Ganem, B. *J. Org. Chem. 48* (1983) 3761.
17. Corriu, R., Escudie, N. and Guerin, C. *J. Organomet. Chem. 264* (1984) 207.
18. Baird, M. S. and Baxter, A. G. W. *J. Chem. Soc., Perkin Trans. 1* (1979) 2317; Taylor, K. G., Hobbs, W. E. and Saquet, M. *J. Org. Chem. 36* (1971) 369; see also Nilsen, N. O., Sydnes, L. K. and Skattebøl, L. *J. Chem. Soc., Chem. Commun.* (1978) 128.
19. Nilsen, N. O., Skattebøl, L., Baird, M. S., Buxton, S. R. and Slowey, P. D. *Tetrahedron Lett.* (1984) 2887.

20. Eisch, J. J. and Gupta, G. *J. Organomet. Chem. 168* (1979) 139; Eisch, J. J. and Foxton, M. W. *J. Org. Chem. 36* (1971) 3520.
21. See e.g., Carter, M. J. and Fleming, I. *J. Chem. Soc. Chem. Commun.* (1976) 79; Fleming, I. and Percival, A. *J. Chem. Soc. Chem. Commun.* (1976) 681; for a more recent route to 1-trimethylsilyl dienes and an extensive bibliography see Ni, Z.-J. and Luh, T. Y. *J. Org. Chem. 53* (1988) 5582.

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