

Reduction of Aryltrimethylsilanes as a Synthetic Method. Part II.¹ Birch Reduction

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Sixteen aryltrimethylsilanes have been reduced by a modification of the Birch reduction (with lithium-ethanol; lithium added last). Along with the expected cyclohexa-1,4-dienes, products of Si-C bond cleavage are also formed, especially when an allylic or benzylic Si-C bond is involved; further reduction to substituted cyclohexenes or cyclohexanes may take place if the primary product contains vinylic trimethylsilyl groups.

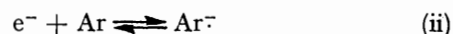
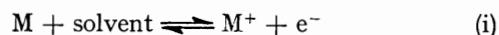
THE Birch reduction² offers more vigorous conditions for the reduction of aryltrialkylsilanes than the electrochemical method described in Part I.¹ Using a variation of the reaction (with lithium-ethanol; lithium added last), we find that at -70° the major products are usually the substituted cyclohexa-1,4-dienes, but at higher temperatures further reduction to cyclohexenes or cyclohexanes may take place. In a number of cases, carbon-silicon bond cleavage occurs with loss of trimethylsilyl groups from the products.

RESULTS AND DISCUSSION

Continuing our investigation of methods for reducing aryltrialkylsilanes, we have investigated a variant of the Birch reduction in which lithium is added in portions to a solution of the organosilicon compound and ethanol in liquid ammonia. Birch^{3a} found that addition of the alkali metal last was beneficial in preventing isomerization of the initially formed diene to the conjugated isomer, which may then be further reduced, though Wilds and Nelson,^{3b} using lithium, obtained better yields in reductions of substituted anisoles by adding the alcohol last.

The ready reduction of the aryl silicon compounds even at -70° is an indication of their high reactivity, which could prove useful, for example, in selective reductions of compounds containing more than one aromatic ring. Aromatic anion radicals are believed to be formed as intermediates in Birch reductions by reversible steps [(i) and (ii)] from the starting materials, followed by an irreversible reaction with the proton donor (iii).† Factors

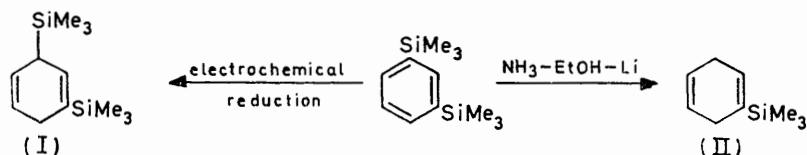
example, by the e.s.r. spectrum of the trimethyl(phenyl)silane radical anion.⁴



↓
reduction products

The results of reduction of sixteen compounds by this method are shown in the Table. The main products, particularly of reactions at -70° , are substituted cyclohexa-1,4-dienes; at -30° further reduction often takes place. The features which distinguish these reactions from the electrochemical reductions considered in Part I¹ are indicated below.

(i) *Cleavage of the (aryl) carbon-silicon bond.* This reaction, which is of minor significance in the electrochemical reduction, assumes greater importance here, particularly when the primary reduction product is a cyclohexa-1,4-diene with an allylic trimethylsilyl group. (The allyl-silicon bond is known to be readily cleaved in basic media.⁵) Thus *m*-bis(trimethylsilyl)benzene, which on electrochemical reduction gives 1,3-bis(trimethylsilyl)cyclohexa-1,4-diene (I) in 74% yield, gives on Birch reduction 82% of cyclohexa-1,4-dienyltrimethylsilane (II), with loss of a trimethylsilyl group. This method thus constitutes a convenient synthesis of (II) [direct electrochemical reduction of trimethyl(phenyl)silane gives cyclohexa-2,5-dienyltrimethylsilane^{1,6}].



which stabilize the anion radical intermediate will produce a larger equilibrium concentration of this species, thus facilitating reduction. That a trimethylsilyl group stabilizes an aromatic anion radical is indicated, for

† Ion pairing and solvation have been ignored for simplicity. For a further discussion and leading references, see ref. 1.

¹ C. Eaborn, R. A. Jackson, and R. Pearce, *J.C.S. Perkin I*, 1974, 2055.

² See, for example, A. J. Birch, *Quart. Rev.*, 1950, **4**, 69; R. G. Harvey, *Synthesis*, 1970, 161.

³ (a) A. J. Birch, *J. Chem. Soc.*, 1946, 593; (b) A. L. Wilds and N. A. Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 5360.

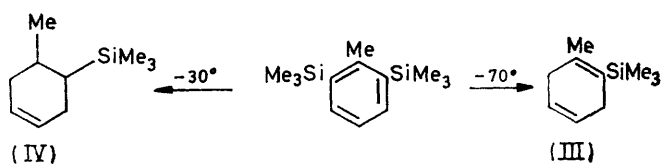
⁴ J. A. Bedford, J. R. Bolton, A. Carrington, and R. H. Prince, *Trans. Faraday Soc.*, 1963, **59**, 53.

⁵ C. Eaborn and R. W. Bott in 'Organometallic Compounds of the Group IV Elements,' vol. 1: 'The Bond to Carbon, Part I,' ed. A. G. MacDiarmid, Dekker, New York, 1968, p. 395.

⁶ R. A. Benkeser and C. A. Tincher, *J. Organometallic Chem.*, 1968, **13**, 139.

ortho-Methyl substituents inhibit the loss of allylic trimethylsilyl groups. Thus, trimethyl-*o*-tolylsilane and 2,6-dimethylphenyltrimethylsilane give predominantly the cyclohexa-1,4-dienes with allylic trimethylsilyl groups, although for the former compound, the presence of the cleavage product 1-methylcyclohexa-1,4-diene among the products is indicated. Trimethyl-*p*-tolylsilane, as expected, gives 1-methyl-4-trimethylsilylcyclohexa-1,4-diene, in which there is a vinylic rather than an allylic trimethylsilyl group.

(ii) *Behaviour of different types of double bond.* At -30° double bonds adjacent to a trimethylsilyl group are reduced, but isolated double bonds are not. At -70° , the major product of reduction of 2,6-bis(trimethylsilyl)toluene is 1-methyl-2-trimethylsilylcyclohexa-1,4-diene (III), but at -30° the predominant product is 4-methyl-5-trimethylsilylcyclohexene (IV). The products formed



from 1-trimethylsilylcyclohexa-1,4-diene, 1,5-bis(trimethylsilyl)cyclohexa-1,4-diene and 1-methyl-2-trimethylsilylcyclohexane are formed in accordance with the same principle. These results are consistent with those of Bock and Seidl,⁷ who find that silyl-substituted olefins and butadienes are more readily reduced than the parent unsaturated compounds.

(iii) *Steric influences.* The probable importance of steric as well as electronic effects in controlling the position of reduction was noted in Part I. The resistance of the aromatic compounds to reduction as far as cyclohexenes is also noteworthy: it implies that cyclohexa-1,3-dienes, which would be further reduced, are not formed in significant amount. Alkylbenzenes show a lower reduction rate, and a greater proportion of cyclohexene in the product, as the alkyl group becomes larger.⁸ This has been attributed to the difficulty of adding the second proton *ortho* to a bulky group (to give the cyclohexa-1,4-diene) with the result that the cyclohexa-1,3-diene is formed instead. The non-formation of cyclohexenes from silyl-substituted aromatic compounds is consistent with the smaller steric hindrance to be expected from the trimethylsilyl than from the *t*-butyl group. However, in the aryltrimethylsilanes, final protonation is at the 1- rather than the 2-position and any comparison should be made with some reservations.

(iv) *Reductions to cyclohexanes.* 1,5-Bis(trimethylsilyl)cyclohexa-1,4-diene and 1-methyl-2-trimethylsilylcyclohexene are both reduced at -30° to cyclohexanes. The preponderance of the thermodynamically less stable isomer in each case is commented on in Part III.⁹

⁷ H. Bock and H. Seidl, *J. Amer. Chem. Soc.*, 1968, **90**, 5694.

⁸ A. P. Krapcho and A. A. Bothner-By, *J. Amer. Chem. Soc.*, 1959, **81**, 3658.

⁹ C. Eaborn, R. A. Jackson, and R. Pearce, following paper.

¹⁰ Ref. 5, p. 402.

(v) *Cleavage of carbon-silicon and silicon-silicon bonds in substituents.* At -30° , (*p*-trimethylsilylbenzyl)trimethylsilane gives as major reduction products two compounds from which the benzylic trimethylsilyl group has been cleaved to leave a methyl group. Benzyltrimethylsilane does not lose its trimethylsilyl group under the same conditions. Cleavage of benzyl-silicon bonds is known to be relatively easy under alkaline conditions,¹⁰ and the presence of a *para*-trimethylsilyl group has been shown to facilitate such cleavages.¹¹ Pentamethyl(phenyl)disilane gave a mixture of cyclohexa-1,4-diene, ethoxytrimethylsilane, and diethoxydimethylsilane under the alkaline conditions of the Birch reduction, in contrast to the electrochemical reduction which gives the 1,4-dihydro-compound as the major product with the pentamethylsilyl group left intact. Silicon-silicon bond cleavages are known to take place under alkaline conditions.¹²

(vi) *Reduction of benzyltrimethylsilane.* This requires more vigorous conditions than are needed for aryltrimethylsilanes, and gives the 2,5- rather than the 1,4-dihydro-product. This accords with the known strong electron-releasing effect of the trimethylsilylmethyl group.¹³

(vii) *Possible intermediacy of dianions.* In reductions of aryltrimethylsilanes, the presence of electron-withdrawing silicon groups might stabilize the dianion sufficiently so that the concentration at equilibrium is no longer vanishingly small as is the case with alkylbenzenes. The reduction of trimethyl(phenyl)silane with lithium in liquid ammonia in the absence of a proton donor was found to proceed, albeit slowly, at -30° . This supports the view that dianions may be intermediates, but the low rate of reduction indicates that they are relatively unimportant in the normal reductions. (The possibility that reduction was effected by adventitious water cannot be ruled out, however, since the ammonia was used without purification.) The observed formation of cyclohexa-2,5-dienyltrimethylsilane and the absence of cyclohexadiene and cyclohexene in the products also indicates that the amide ion is less effective than the ethoxide ion in promoting cleavage of the aryl-silicon bond.

N.m.r. and I.r. Spectra. Some general features of interest in the compounds obtained by reduction of aryltrimethylsilanes are: (a) The ethylenic proton resonances show a downfield shift in the n.m.r. spectra when the double bond bears a trimethylsilyl substituent. Similar effects have been observed in acyclic systems and interpreted on the basis of a (*p* \rightarrow *d*) _{π} interaction between the double bond and the silicon atom.⁷ (b) Protons attached to a saturated carbon atom bearing a trimethylsilyl substituent show an upfield shift in the n.m.r. spectra. (c) In the i.r. spectra, there is a shift to lower wavenumber and intensification of the C=C stretching frequency upon substitution by a trimethylsilyl group.

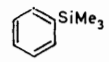
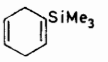
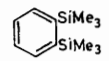
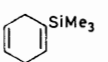
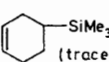
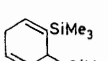
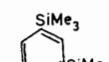
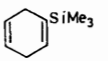
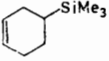
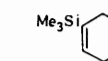
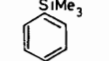
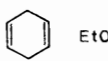
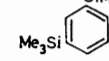
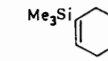
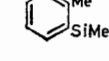
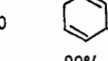
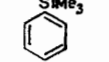
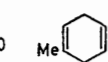
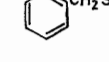
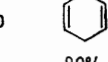
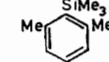
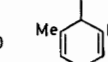
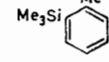
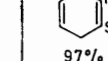
¹¹ C. Eaborn and S. H. Parker, *J. Chem. Soc.*, 1955, 126.

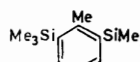
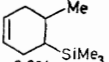
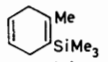
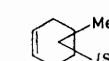
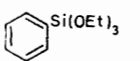

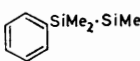

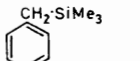
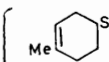
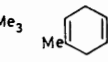
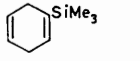
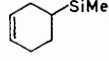
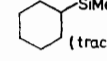
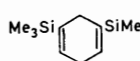
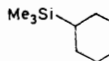
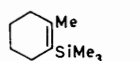
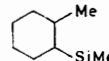
¹² M. Kumada, K. Tamao, M. Ishikawa, and M. Matsuno, *Chem. Comm.*, 1968, 614.

¹³ C. Eaborn and S. H. Parker, *J. Chem. Soc.*, 1954, 939; C. Eaborn, *ibid.*, 1956, 4858.

Again similar effects have been observed in acyclic systems, and attributed to ($p \rightarrow d$) π bonding.⁷ (d) Compounds containing the 3-trimethylsilylcyclohexa-1,4-

Birch reduction of aryltrimethylsilanes and other compounds

Starting material	Reaction temp. (°C)	Products isolated or detected, with relative yields	% Isolated
	-70	 <i>a</i>	5
	-70	  (trace)	38
		 94%	4.6
	-70	 96%  4%	85
		 <i>b</i>	ca. 3
	-30	 EtOSiMe ₃ <i>c</i>	
	70		85
	-70	 <i>d</i>	60
	-70	 95%	58
	-30	 90%	68
	-70		70
	-70	 97%	55
		3 major components, thought to be di- or tetra-hydro-derivatives of starting material	33

Starting material	Reaction temp. (°C)	Products isolated or detected, with relative yields	% Isolated
	-30	 96%  4%	52
		 (3 major components)	18
	-70	 (EtO) ₂ Si	77 of (EtO) ₂ Si
	-70	 EtOSiMe ₃ (EtO) ₂ SiMe ₂	
	-30	 	65
		Fraction b. p. 60–61° at 0.35 mmHg (2 major components)	8
	-30	  (trace)	86
	-30	 <i>cis</i> : <i>trans</i> 43:57	75
	-30	 <i>cis</i> : <i>trans</i> 60:40	66

^a Ethoxytrimethylsilane and cyclohexa-1,4-diene detected by g.l.c. ^b Impure: contained 1,3-bis(trimethylsilyl)cyclohexane in proportions (*cis*:*trans*) 45:55. ^c Reaction slow at -70°. ^d Presence indicated of 1-methylcyclohexa-1,4-diene in forerun. ^e Prepared *in situ* from 1,3,5-tris(trimethylsilyl)benzene.

diene grouping show a characteristic i.r. absorption at ca. 1100 cm⁻¹.

EXPERIMENTAL

Gas chromatography and spectroscopic measurements were carried out as described in Part I.¹

Reduction of Arylsilicon Compounds with Lithium and Ethanol in Liquid Ammonia (Birch Reduction).—General method. Reactions were carried out in a two-necked flask (250 or 500 ml) fitted with a cold-finger condenser (ethanol-solid CO₂) and magnetic stirrer. The apparatus was assembled hot and flushed with nitrogen prior to the addition of the arylsilicon compound (ca. 0.01 mol) and ethanol (in excess); ammonia (ca. 200 ml) was then condensed in. The reaction was carried out under nitrogen either without cooling (for reaction at -30°) or with the flask cooled in an ethanol-solid CO₂ bath (for reaction at -70°). Lithium was added in ca. 0.05 g portions until the blue colouration was no longer discharged. The ammonia was evaporated off and the residue extracted with water and ether. The ethereal layer was separated, the aqueous layer was extracted with ether (2 × 10 ml), and the combined extracts

were dried (MgSO_4). Fractionation (80 cm Vigreux column) afforded the products as colourless liquids. Prepared by this method were the following:

Cyclohexa-1,4-dienyltrimethylsilane. 1,3-Bis(trimethylsilyl)benzene (7.16 g, 0.032 mol), ethanol (20 ml), and lithium (0.88 g, 0.126 g atom) gave (at -70°): (i) *cyclohexa-1,4-dienyltrimethylsilane* (4.1 g, 85%), b.p. 67° at 17 mmHg, n_D^{25} 1.4720 (Found: C, 70.7; H, 10.8. $\text{C}_9\text{H}_{16}\text{Si}$ requires C, 71.0; H, 10.6%); m/e 152; λ_{max} (hexane) 223 nm; ν_{max} 1672w and 1618m cm^{-1} ; τ 3.95 (1H, m), 4.25 (2H, m), 7.28 (4H, m), and 9.92 (9H, s) [g.l.c. (ODPN) showed the presence of cyclohex-3-enyltrimethylsilane (4%)]]; (ii) a fraction, b.p. $60-63^\circ$ at 0.1 mmHg (0.23 g), which was later shown (g.l.c.) to contain 1,5-bis(trimethylsilyl)cyclohexa-1,4-diene and *cis*- and *trans*-1,3-bis(trimethylsilyl)cyclohexane (45 : 55). Ethoxytrimethylsilane was present in the forerun (g.l.c.).

1,6-Bis(trimethylsilyl)cyclohexa-1,4-diene. 1,2-Bis(trimethylsilyl)benzene (6.0 g, 0.027 mol), ethanol (20 ml), and lithium (0.53 g, 0.076 g atom) gave (at -70°): (i) cyclohexa-1,4-dienyltrimethylsilane (1.55 g, 38%); (ii) 1,6-bis(trimethylsilyl)cyclohexa-1,4-diene (2.8 g, 46%), b.p. 56° at 0.75 mmHg, n_D^{25} 1.4850 (Found: C, 64.4; H, 10.8. $\text{C}_{12}\text{H}_{24}\text{Si}_2$ requires C, 64.2; H, 10.8%); λ_{max} (hexane) 223 nm; ν_{max} 1650w, 1588m, and 1105s cm^{-1} ; τ 4.0—4.3 (3H, m), 7.2—7.5 (3H, m), and 9.83 and 9.90 (18H, two s). G.l.c. (Ucon oil) showed the presence of ca. 3% of an unidentified compound and ca. 3% of 1,2-bis(trimethylsilyl)benzene.

1,5-Bis(trimethylsilyl)cyclohexa-1,4-diene. 1,3,5-Tris(trimethylsilyl)benzene (2.73 g, 0.0096 mol), ethanol (10 ml), and lithium (0.39 g, 0.055 g atom) gave (at -70°) 1,5-bis(trimethylsilyl)cyclohexa-1,4-diene (1.75 g, 85%), b.p. 64° at 0.65 mmHg, n_D^{25} 1.4735 (Found: C, 64.3; H, 10.95. $\text{C}_{12}\text{H}_{24}\text{Si}_2$ requires C, 64.2; H, 10.8%); m/e 224; ν_{max} 1645m and 1607m cm^{-1} ; τ 3.9 (2H, m), 7.28 (4H, m), and 9.92 (18H, s).

cis- and *trans*-1,3-Bis(trimethylsilyl)cyclohexane. 1,3,5-Tris(trimethylsilyl)benzene (3.0 g, 0.01 mol), ethanol (15 ml), and lithium (1.1 g, 0.16 g atom) gave (at -30°) a fraction (1.7 g, 75%), b.p. 53° at 0.6 mmHg. G.l.c. showed the presence of two components [(A) and (B)], with relative retention times of 0.83 : 1 (Ucon oil) and 0.90 : 1 (SE30), in relative yields of 43 and 57%, respectively. Preparative g.l.c. (Ucon oil) afforded (A) and (B) as colourless liquids. *cis*-1,3-Bis(trimethylsilyl)cyclohexane (A) had n_D^{25} 1.4550 (Found: C, 63.8; H, 12.5. $\text{C}_{12}\text{H}_{28}\text{Si}_2$ requires C, 63.1; H, 12.35%); τ 7.8—9.1vbr (10H, m) and 10.01 (18H, s). *trans*-1,3-Bis(trimethylsilyl)cyclohexane (B) had n_D^{25} 1.4580 (Found: C, 63.5; H, 12.5%); τ 8.4 (8H, m), 9.1—9.2 (2H, m), and 9.94 (18H, s). The n.m.r. spectra were essentially invariant from 25 to -80° . Assignments of stereochemistry are considered in Part III.⁹

trans- and *cis*-Trimethyl-(2-methylcyclohexyl)silane. Trimethyl-(2-methylcyclohex-1-enyl)silane (see later) (3.3 g, 0.02 mol), ethanol (10 ml), and lithium (0.55 g, 0.08 g atom) gave (at -30°) a fraction, b.p. $74-75^\circ$ at 14 mmHg (2.2 g, 66%) (Found: C, 70.5; H, 12.9. $\text{C}_{10}\text{H}_{22}\text{Si}$ requires C, 70.5; H, 13.0%). G.l.c. showed the presence of two components [(C) and (D)] with relative retention times of 0.91 : 1 (Ucon oil) and 0.92 : 1 (SE30), in relative yields of 40 and 60%, respectively. Preparative g.l.c. (Ucon oil, 40×30 μl samples) afforded (C) and (D) as colourless liquids (purity >98%). *trans*-Trimethyl-(2-methylcyclohexyl)silane (C) had n_D^{25} 1.4531; τ 8.2—9.2br (13H, m with s at τ 9.04), 10.00 (9H, s). *cis*-Trimethyl-(2-methylcyclohexyl)silane (D) had

n_D^{25} 1.4552; τ 8.5 (9H, m), 9.03 (4H, d superimposed on weak m, J_d 7 Hz), and 10.00 (9H, s). Assignments of stereochemistry are considered in Part III.⁹

Trimethyl-(2-methylcyclohexa-2,5-dienyl)silane. Trimethyl-*o*-tolylsilane (10.5 g, 0.064 mol), ethanol (20 ml), and lithium (1.20 g, 0.17 g atom) gave (at -70°) trimethyl-(2-methylcyclohexa-2,5-dienyl)silane (6.3 g, 60%), b.p. $74-75^\circ$ at 15 mmHg, n_D^{25} 1.4798 (Found: C, 72.3; H, 10.9. $\text{C}_{10}\text{H}_{18}\text{Si}$ requires C, 72.2; H, 10.9%); ν_{max} 1675w, 1630w, and 1100s cm^{-1} ; τ 4.3 (2H, m), 4.7br (1H, m), 7.4br (2H, m), 7.9br (1H, m), 8.33 (3H, m), and 9.94 (9H, s). G.l.c. (ODPN) showed the presence of ca. 10% impurities. The presence of 1-methylcyclohexa-1,4-diene was indicated in the fore-run (i.r.).

Cyclohexa-1,4-dienylmethyltrimethylsilane. Benzyltrimethylsilane (5.0 g, 0.033 mol), ethanol (10 ml), and lithium (1.0 g, 0.14 mol) gave (at -30°) cyclohexa-1,4-dienylmethyltrimethylsilane (3.4 g, 68%), b.p. $70-71^\circ$ at 9.5 mmHg, n_D^{25} 1.4736 (Found: C, 72.3; H, 11.0. $\text{C}_{10}\text{H}_{18}\text{Si}$ requires C, 72.2; H, 10.9%); ν_{max} 1685w and 1640w cm^{-1} ; τ 4.34 (2H, m), 4.76 (1H, m), 7.4 (4H, m), 8.58br (2H, s), and 10.00 (9H, s). G.l.c. (ODPN) showed the presence of ca. 10% impurities. (Reaction at -70° was extremely slow.)

Trimethyl-(4-methylcyclohexa-1,4-dienyl)silane. Trimethyl-*p*-tolylsilane (10.4 g, 0.07 mol), ethanol (20 ml), and lithium (1.1 g, 0.16 g atom) gave (at -70°) trimethyl-(4-methylcyclohexa-1,4-dienyl)silane (5.8 g, 58%), b.p. 73° at 9.5 mmHg, n_D^{25} 1.4740 (Found: C, 72.3; H, 11.05. $\text{C}_{10}\text{H}_{18}\text{Si}$ requires C, 72.2; H, 10.9%); ν_{max} 1690w and 1620m cm^{-1} ; τ 4.0 (1H, m), 4.5 (1H, m), 7.35 (4H, m), 8.33 (3H, m), and 9.92 (9H, s). G.l.c. (ODPN) showed the presence of ca. 5% of impurities (mainly trimethyl-*p*-tolylsilane).

Trimethyl-(2-methylcyclohexa-1,4-dienyl)silane. 2,6-Bis(trimethylsilyl)toluene (17.0 g, 0.051 mol), ethanol (25 ml), and lithium (1.5 g, 0.21 g atom) gave (at -70°): (i) trimethyl-(2-methylcyclohexa-1,4-dienyl)silane (6.5 g, 55%), b.p. 75° at 10 mmHg, n_D^{25} 1.4863 (Found: C, 72.4; H, 10.9. $\text{C}_{10}\text{H}_{18}\text{Si}$ requires C, 72.2; H, 10.9%); ν_{max} 1680w and 1625m cm^{-1} ; τ 4.25 (2H, m), 7.3 (4H, m), 8.20 (3H, m), and 9.80 (9H, s). G.l.c. (ODPN) showed the presence of ca. 3% of impurities; (ii) a fraction (5.6 g, 33%), b.p. $46-51^\circ$ at 0.15 mmHg; g.l.c. (SE30) showed the presence of three unresolved components; ν_{max} 1660w, 1605m, and 1110m cm^{-1} , indicating the presence of $\text{C}=\text{C}-\text{SiMe}_3$ and $[\text{C}]_2\cdot\text{CH}\cdot\text{SiMe}_3$ functions.

2,6-Dimethylcyclohexa-2,5-dienyltrimethylsilane. 2,6-Dimethylphenyltrimethylsilane (2.3 g, 0.013 mol), ethanol (10 ml), and lithium (0.28 g, 0.04 g atom) gave (at -70°) 2,6-dimethylcyclohexa-2,5-dienyltrimethylsilane (1.6 g, 70%), b.p. $75-76^\circ$ at 8 mmHg, n_D^{25} 1.4842 (Found: C, 73.3; H, 11.35. $\text{C}_{11}\text{H}_{20}\text{Si}$ requires C, 73.25; H, 11.2%); ν_{max} 1680w and 1105m cm^{-1} ; τ 4.7br (2H, m), 7.4br (2H, m), 7.92 (1H, t, J 4 Hz), 8.23 (6H, partially resolved q), and 9.87 (9H, s).

Trimethyl-(2-methylcyclohex-4-enyl)silane. 2,6-Bis(trimethylsilyl)toluene (5.3 g, 0.022 mol), ethanol (12 ml), and lithium (0.93 g, 0.13 g atom) gave (at -30°): (i) trimethyl-(2-methylcyclohex-4-enyl)silane (1.9 g, 52%), b.p. $75-76^\circ$ at 16 mmHg, n_D^{25} 1.4651 (Found: C, 71.3; H, 12.3. $\text{C}_{10}\text{H}_{20}\text{Si}$ requires C, 71.3; H, 12.0%); ν_{max} 1660w and 1650w cm^{-1} ; τ 4.35 (2H, m), 7.8—8.5br (5H, m), 9.0—9.2br (4H, m), and 10.00 (9H, s); g.l.c. showed the presence of trimethyl-2-methylcyclohexa-1,4-dienylsilane (ca. 4%); (ii) a fraction (1.0 g, 18%), b.p. $50-52^\circ$ at 0.07 mmHg; g.l.c. (SE30) showed the presence of three unresolved components; ν_{max} 1610m cm^{-1} indicating the presence of the $\text{C}=\text{C}-\text{SiMe}_3$ function.

Reduction of trimethyl(phenyl)silane. Trimethyl(phenyl)silane (10.1 g, 0.068 mol), ethanol (25 ml), and lithium (1.2 g, 0.17 g atom) gave (at -70°) cyclohexa-1,4-dienyltrimethylsilane (0.53 g, 5%). Physical properties (b.p., i.r. spectrum, and n_D^{25}) were identical with those of the previously prepared sample. G.l.c. (Ucon oil) of the ethereal solution before fractionation showed the presence of ethoxytrimethylsilane and cyclohexa-1,4-diene as major products with traces of cyclohexene and hexamethyldisiloxane.

Reduction of 1,4-bis(trimethylsilyl)benzene. G.l.c. (Ucon oil) of the ethereal extract from the reaction between 1,4-bis(trimethylsilyl)benzene (5.1 g, 0.024 mol), ethanol (15 ml), and lithium (1.23 g, 0.18 g atom) (at -30°) showed the presence of ethoxytrimethylsilane and cyclohexa-1,4-diene as the only major products. (Reaction at -70° was very slow.)

Reduction of cyclohexa-1,4-dienyltrimethylsilane. This compound (4.0 g, 0.026 mol), ethanol (10 ml), and lithium (0.60 g, 0.085 g atom) gave (at -30°) cyclohex-3-enyltrimethylsilane (3.45 g, 86%), b.p. 83° at 39 mmHg (lit.,¹⁴ 175° at 760 mmHg). G.l.c. (ODPN) showed the presence of cyclohexyltrimethylsilane (ca. 0.5%).

Reduction of triethoxy(phenyl)silane. Triethoxy(phenyl)silane (12.9 g, 0.054 mol), ethanol (20 ml), and lithium (1.6 g, 0.23 g atom) gave (at -70°): (i) a fraction, b.p. $75-80^\circ$ at 30 mmHg (8.6 g, 77%), which was shown to be mainly tetraethoxysilane (by g.l.c.) (lit.,¹⁵ b.p. 166° at 765 mmHg), (ii) a fraction, b.p. $71-72^\circ$ at 0.8 mmHg (0.2 g), which contained three major components (g.l.c. on SE30).

Reduction of pentamethyl(phenyl)disilane. Pentamethyl(phenyl)disilane (4.8 g, 0.023 mol), ethanol (10 ml), and lithium (0.50 g, 0.07 g atom) gave (at -70°) a fraction, b.p. $110-112^\circ$ at 760 mmHg. The compound (pure by g.l.c.) was indicated by its i.r. spectrum to be diethoxydimethylsilane (lit.,¹⁶ b.p. 114° at 760 mmHg). G.l.c. (Ucon oil) of the forerun showed the presence of ethoxytrimethylsilane and cyclohexa-1,4-diene as major products.

Reduction of trimethyl-(p-trimethylsilylbenzyl)silane. Trimethyl-(p-trimethylsilylbenzyl)silane (5.0 g, 0.021 g atom),

ethanol (10 ml), and lithium (1.0 g, 0.14 g atom) gave (at -30°): (i) a fraction, b.p. $86-88^\circ$ at 21 mmHg (2.35 g, 65%). G.l.c. (Ucon oil) showed the presence of trimethyl-(4-methylcyclohexa-1,4-dienyl)silane and one other component. Preparative g.l.c. (Ucon oil) separated this binary mixture. The other component was trimethyl-(4-methylcyclohex-3-enyl)silane, n_D^{25} 1.4609 (Found: C, 71.65; H, 12.25. $C_{10}H_{20}Si$ requires C, 71.3; H, 12.0%); ν_{max} 1680 cm^{-1} ; τ 4.5 (1H, m), 7.8—8.4 (ca. 8H, two m, centred at 8.0 and 8.3), 8.4—9.5vbr (ca. 2H, m), and 10.00 (9H, s); (ii) a fraction (0.4 g, 8%), b.p. $60-61^\circ$ at 0.35 mmHg; g.l.c. (Ucon oil) showed two major components (not starting material); ν_{max} 1670 cm^{-1} and 1620 cm^{-1} . (Reduction at -70° was very slow.)

Reduction of trimethyl(phenyl)silane in the absence of ethanol. Trimethyl(phenyl)silane (3 g) and lithium (0.1 g) in liquid ammonia (100 ml) were stirred at reflux for 4 h. The blue colouration was not discharged. Ammonium chloride was added to destroy the excess of lithium, and g.l.c. of the ethereal extract showed the presence of cyclohexa-2,5-dienyltrimethylsilane [ca. 20% with respect to the recovered trimethyl(phenyl)silane] and cyclohex-3-enyltrimethylsilane (trace). No cyclohexene or cyclohexa-1,4-diene was present.

Trimethyl-(2-methylcyclohex-1-enyl)silane. Hydrogenation of trimethyl-(2-methylcyclohexa-1,4-dienyl)silane (10 g) in ethanol (100 ml) over Adams catalyst (ca. 0.1 g) afforded a fraction (9.5 g, 95%), b.p. 69° at 9 mmHg. G.l.c. (Ucon oil) showed the presence of two components, trimethyl-(2-methylcyclohex-1-enyl)silane and trimethyl-o-tolylsilane (ca. 20%). Preparative g.l.c. (Ucon oil) gave trimethyl-2-methylcyclohex-1-enyl silane, n_D^{25} 1.4768 (Found: C, 71.9; H, 12.1. $C_{10}H_{20}Si$ requires C, 71.3; H, 12.0%); ν_{max} 1623 cm^{-1} ; τ 8.0 (4H, m), 8.25 (3H, m), 8.4 (4H, m), and 9.88 (9H, s).

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