

## Reduction of Aryltrimethylsilanes as a Synthetic Method. Part I. Electrochemical Reduction

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Electrochemical reduction of aryltrimethyl-silanes and -germanes affords a convenient preparative route to silyl- and germyl-substituted cyclohexa-1,4-dienes, since in most cases the products resist further reduction. The nature of the products is in accord with a Birch-type reduction mechanism. Trimethyl(phenyl)silane gives cyclohexa-2,5-dienyltrimethylsilane in 79% yield. The three bis(trimethylsilyl)benzene isomers and trimethyl-*m*-tolylsilane give the isomers predicted on the basis of the electronic effects of the substituent groups, but trimethyl-*p*-tolylsilane, in which the directing effects conflict, gives a mixture of products. Steric as well as electronic influences are probably important. Trialkyl(phenyl)germanes behave analogously to trimethyl(phenyl)silane, but trimethyl(phenyl)tin undergoes cleavage of the tin-carbon bond. The two stereoisomers of 3,6-bis(trimethylsilyl)cyclohexa-1,4-diene were isolated and tentatively assigned configurations.

ARYLTRIALKYL-SILANES AND -GERMANES are easily prepared, and so specific reduction procedures which would give fully or partially reduced compounds would be of considerable synthetic utility. This series of three papers will describe the application of three such methods in increasing order of reducing power. Parts II and III will report on two modifications of the Birch procedure; the present paper deals with an electrochemical reduction, which gives mainly the substituted cyclohexa-1,4-dienes. Advantages from the synthetic point of view include the avoidance of the use of metallic lithium or basic media, which are unacceptable in some situations.

### RESULTS AND DISCUSSION

Methods of synthesis of trialkylsilyl-substituted cyclohexa-1,4-dienes include electrochemical<sup>1</sup> or Birch<sup>2</sup> reduction of the corresponding trialkylarylsilanes. Disilyl-substituted compounds can be prepared directly from the unsubstituted aromatic compounds by reductive silylation (see, for example, refs. 3—5). Since the products of these reactions usually contain allylic trialkylsilyl groups, such groups can be removed subsequently to give the unsubstituted cyclohexa-1,4-diene in good yield, which further enhances the synthetic utility of the method.<sup>5</sup>

In this paper we report the results of electrochemical reductions of organosilyl- and organogermyl-substituted aromatic compounds. The reactions were carried out in methylamine-lithium chloride solution between platinum gauze electrodes, in an apparatus essentially similar to the 'undivided electrolysis cell' described by Benkeser and his co-workers.<sup>6</sup> The products obtained by reduction of twelve compounds by this method are listed in the Table.

The predominant reduction product of the aromatic compounds is normally a cyclohexa-1,4-diene. Of the various possible isomeric products, one is normally predominant; for example, reduction of trimethyl(phenyl)silane gives cyclohexa-2,5-dienyltrimethylsilane in 79% yield, in agreement with the observation of Benkeser and Tincher,<sup>1</sup> with only minor amounts of

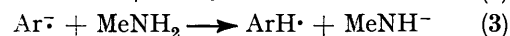
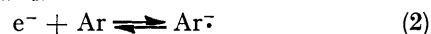
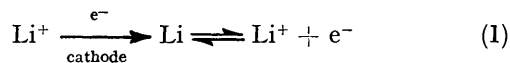
<sup>1</sup> R. A. Benkeser and C. A. Tincher, *J. Organometallic Chem.*, 1968, **13**, 139.

<sup>2</sup> H. Alt, E. R. Franke, and H. Bock, *Angew. Chem. Internat. Edn.*, 1969, **8**, 525.

<sup>3</sup> D. R. Weyenberg and L. H. Toporcer, *J. Amer. Chem. Soc.*, 1962, **84**, 2843.

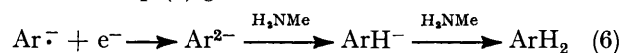
the 1,4-isomer and products of further reduction. This point is considered further in the following discussion of mechanism. Trialkyl(phenyl)germanes behave analogously to the silicon compounds, but with trimethyl(phenyl)tin cleavage of the tin-phenyl bond was found to occur.

*Mechanism.*—It was suggested by Benkeser and his co-workers<sup>6</sup> that the reduction of aromatic compounds in this type of electrolysis system was probably effected by lithium, itself formed by cathodic reduction. A mechanism similar to that established for the Birch reduction may thus reasonably be postulated, as outlined in equations (1)—(5). (For simplicity, solvation and ion-pairing have been neglected.)



A transient colour at the cathode was noted, ranging from green-yellow to deep blue according to the compound being electrolysed and possibly due to the presence of radical anions. At the conclusion of the reductions, the characteristic blue colour of lithium in alkylamines was observed.

This scheme, or the alternative scheme in which a dianion is involved [reaction (6) instead of (3)—(5)], is consistent with the products formed. The first electron-transfer step (2) gives a radical ion in which an electron



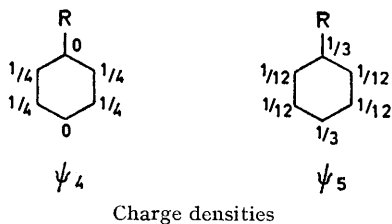
must occupy an antibonding orbital. The two lowest lying antibonding orbitals, designated  $\psi_4$  and  $\psi_5$  are degenerate in benzene, but the degeneracy is lifted if a substituent is present: electron-withdrawing substituents lower the energy of  $\psi_5$  (since there is charge density at position 1) whereas electron-releasing substituents lower the energy of  $\psi_4$ .

<sup>4</sup> T. Brennan and H. Gilman, *J. Organometallic Chem.*, 1968, **12**, 291.

<sup>5</sup> J. Dunoguès, R. Calas, and N. Ardoin, *J. Organometallic Chem.*, 1972, **43**, 127.

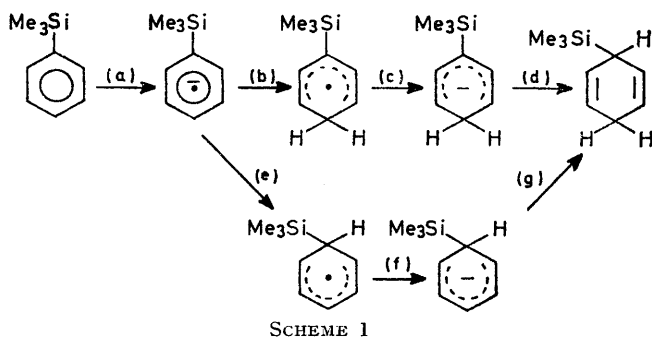
<sup>6</sup> R. A. Benkeser and E. M. Kaiser, *J. Amer. Chem. Soc.*, 1963, **85**, 2858; R. A. Benkeser, E. M. Kaiser, and R. F. Lambert, *ibid.*, 1964, **86**, 5272.

The results of e.s.r. studies of radical anions accord with this: alkyl substituents (R) give rise to spectra



consistent with location of the unpaired electron in  $\psi_4$ , whereas in trimethylsilylbenzene  $\psi_5$  appears to be occupied.<sup>7</sup> If we assume that protonation takes place at the position of highest charge density, this suggests *ortho*- or *meta*-attack for alkylbenzenes, giving rise eventually to 1-alkylcyclohexa-1,4-dienes (as actually occurs<sup>6</sup>), but *para*-attack for trimethyl(phenyl)silane.

The attack by the second proton must be considered to be irreversible, since otherwise the thermodynamically more favoured conjugated dienes would be expected. Attack takes place at a position *para* to the point of attachment of the first proton, as happens in other instances. This position can be calculated, in the unsubstituted cyclohexadienyl anion at least,<sup>8a</sup> to be the site of highest electron density, thereby favouring attack by a proton at this position, giving the non-conjugated diene. Alternatively, the 'principle of least motion'



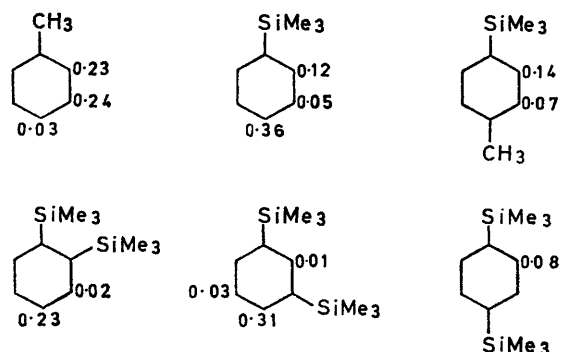
has been invoked to provide at least part of the explanation of why the thermodynamically less favoured non-conjugated diene is formed.<sup>8b</sup> If the dianion route (b) were followed, theory would predict the same products.<sup>8a</sup> Initial protonation at the 1-position [(a), (e), (f), and (g) in Scheme 1] would give rise to the same products.

The products formed on reduction of *o*-, *m*-, and *p*-bis(trimethylsilyl)benzene accord with this picture: initial protonation at the positions of highest electron density (Scheme 2) followed by electron transfer and addition of a second proton at a position '*para*' to the first [for the reasons discussed above for trimethyl(phenyl)silane] would account for the major products observed (see Table). The single product formed on reduction of trimethyl-*m*-tolylsilane is that expected on the basis of a combination of the concordant effects of the methyl and the trimethylsilyl groups.

<sup>7</sup> J. A. Bedford, J. R. Bolton, A. Carrington, and R. H. Prince, *Trans. Faraday Soc.*, 1963, **59**, 53.

Our results suggest that steric hindrance to protonation may also be important in trimethylsilyl-substituted systems. In trimethyl-*p*-tolylsilane, the electronic effect of the trimethylsilyl group is in opposition to that of the methyl group. The electron densities shown in Scheme 2 suggest that the electronic influence of the trimethylsilyl group is the stronger, yet at  $-5^\circ$  the products of 1,4- and 2,5-addition are formed in roughly equal amounts, and at  $-50^\circ$  2,5-addition (expected if the methyl group were dominant) predominates. This suggests the importance of steric

SCHEME 2  
Charge densities for various substituted benzene radical anions\*



\* E.s.r. data from ref. 7 and from J. R. Bolton and A. Carrington, *Mol. Phys.*, 1961, **4**, 497; A. L. Allred and L. W. Bush, *J. Amer. Chem. Soc.*, 1968, **90**, 3352; and F. Gerson, J. Heinzer, H. Bock, H. Alt, and H. Seidl, *Helv. Chim. Acta*, 1968, **51**, 707. A value of 22.5 has been used for  $Q$  in McConnell's expression.


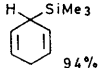
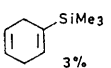
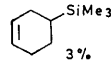
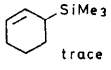

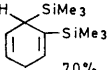
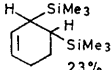
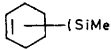

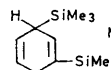
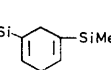
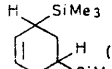




















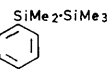
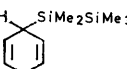


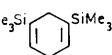
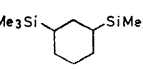
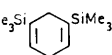
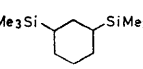
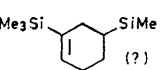
influences: the 2- and 5-positions are more accessible than the 1- and 4-positions. The fact that at  $-50^\circ$  reduction of *p*-bis(trimethylsilyl)benzene is not complete, whereas trimethyl-*p*-tolylsilane is completely reduced (with preponderant addition at the 2- and 5-positions) is another indication of the importance of steric effects in determining the site and rate of protonation.

Little further attack takes place in the case of trimethyl(phenyl)silane, since the cyclohexa-2,5-dienyltrimethylsilane formed as the initial product is much less easily reduced than the parent compound. The product is essentially an internal olefin, which should be much more difficult to reduce than an aromatic compound. The same behaviour is found for compounds such as *p*-bis(trimethylsilyl)benzene and trimethyl-*m*-tolylsilane, which give non-conjugated diene products containing no vinylic trimethylsilyl groups. However, for compounds such as *o*-bis(trimethylsilyl)benzene and trimethyl-*p*-tolylsilane, for which the primary reduction products include compounds with vinylic trimethylsilyl groups, further reduction of the relevant double bond takes place. (Trimethylsilyl-substituted olefins and butadienes are known to be more readily reduced than the corresponding parent olefins.<sup>9,10</sup>) This point will be discussed further in Part II.

<sup>8</sup> (a) H. E. Zimmerman, *Tetrahedron*, 1961, **16**, 169; (b) J. Hine, *J. Org. Chem.*, 1966, **31**, 1236.

<sup>9</sup> R. West, 153rd A.C.S. Meeting, Florida, 1967, L064.

<sup>10</sup> H. Bock and H. Seidl, *J. Amer. Chem. Soc.*, 1968, **90**, 5694.

Starting material	Reaction temp. (°C)	Electrochemical reductions Products, with relative yields	Total yield of products (%)	Comments
	-5	 94%  3%  3%  trace	84	See also ref. 1
	-50	 70%  23%  (SiMe <sub>3</sub> ) <sub>2</sub> 6%	75	Contained <i>ca.</i> 1% of an unidentified compound
	-50	 91%  <i>ca.</i> 1%	75	Contained additionally  (?) 8%
	-5	 <i>cis</i> : <i>trans</i> 78 : 20	93	Contained 2% of an unidentified compound
	-50	 <i>cis</i> : <i>trans</i> 85 : 15		
	-5		50	
	-5		80	
	-40	 , Me <sub>3</sub> SnH, and Me <sub>3</sub> SnOH		
	-5		75	
	-5	 <i>cis</i> 27%  <i>trans</i> 27%  26%  20%	75	
	-50	 <i>cis</i> 29%  <i>trans</i> 9%  6%  56%		
	-5		76	
	-5			Reduction incomplete
	-5			Reduction incomplete; contained <i>ca.</i> 10%
	-5	 <i>cis</i> : <i>trans</i> 1:9  (?)		

The formation of the non-conjugated dienes implies that addition of the second proton is kinetically controlled. This inference is supported by the stereochemistry of the products. In *p*-bis(trimethylsilyl)benzene there is a marked preponderance of the *cis*-isomer, especially at the lower temperature, which



implies that approach of the proton donor takes place at the less hindered side of the intermediate anion (I). Stereoselectivity is lower in trimethyl-*p*-tolylsilane, for which steric hindrance to protonation in the anion will be less important.

*Assignment of Stereochemistry.*—The diene products of reduction of *p*-bis(trimethylsilyl)benzene and of trimethyl-*p*-tolylsilane were mixtures of the *cis*- and *trans*-isomers in each case. These were separated, and stereochemistries were assigned on the basis of the following considerations. (a) In hydrogenation, with Adams catalyst in ethanol, one stereoisomer in each pair was reduced more rapidly than the other. It has been found that in the hydrogenation of substituted cyclohexenes the orientation of the final product is sensitive to substituents removed from the double bond, indicating that steric hindrance to co-ordination at the catalyst surface is important.<sup>11</sup> Models show that effective co-ordination of the double bonds with the catalyst surface will be hindered in the *trans*- but not the *cis*-compound. On this basis, the isomers which are hydrogenated faster are tentatively assigned *cis*-structures and these assignments are used in the remainder of this discussion. (b) In the compound assigned as *cis*-6-methyl-3-trimethylsilylcyclohexa-1,4-diene, the appearance of the H-3 resonance as a doublet of triplets (the *trans*-compound gave a poorly resolved multiplet) is in accord with the larger doublet coupling constant found in *cis*- (as opposed to *trans*-) 3-phenyl-6-triphenylmethylcyclohexa-1,4-diene, for which structures have been established by thermodynamic and X-ray methods.<sup>12</sup> Unfortunately, no correlation could be established between the chemical shifts of the various protons in our compounds and those reported for other cyclohexa-1,4-dienes.<sup>12-15</sup> (c) The relative g.l.c. retention times of the two geometrical isomers of each of our cyclohexa-1,4-dienes were measured on a non-polar and on a polar column. In general, for compounds having only subtle differences in structure, retention times on a non-polar column are a function of b.p., but on a polar column, they are a function of b.p. and 'polarity'. Specific interactions of the stationary phase with the double bonds (the polar functions) of the cyclohexadienes would be expected to be greater for the more accessible

*cis*- than for the less accessible *trans*-isomer. In accord with this, we find that in both cases there is an increase in the ratio (retention time for the *cis*-isomer) : (retention time for the *trans*-isomer) on going from a less polar to a more polar column. However, we find that the *cis*-isomers have greater retention times than the *trans*-isomers, whereas the reverse has been reported for 1',4'-dihydroterphenyls.<sup>14</sup> (d) *trans*-3,6-Bis(trimethylsilyl)cyclohexa-1,4-diene is a solid, whereas its *cis*-isomer is a liquid. This accords with the observations by Harvey *et al.*<sup>14</sup> that for 1',4'-dihydroterphenyls the *trans*-isomers have higher m.p.s, but is in conflict with the sequence of m.p.s of the rather less similar 3-phenyl-6-triphenylmethylcyclohexa-1,4-dienes.<sup>16</sup> (e) The *cis*-compounds are more easily oxidised by air to the aromatic compounds. This accords with observations by Harvey *et al.*<sup>14</sup> on 1',4'-dihydroterphenyls, though they used other oxidising agents.

Our observations on the relative stabilities of the two isomers of 3,6-bis(trimethylsilyl)cyclohexa-1,4-diene led us to repeat the experiment of Weyenberg and Toporcer.<sup>3</sup> We stirred a mixture of benzene, lithium, and chlorotrimethylsilane in tetrahydrofuran at 0° under argon, and analysed samples at intervals by g.l.c. The initial products appeared to be the *cis*- and *trans*-isomers of 3,6-bis(trimethylsilyl)cyclohexa-1,4-diene, with a marked preponderance of the *trans*-isomer (*cis* : *trans*, 1 : 3). After about 5 h, the formation of these compounds was essentially complete; subsequently the amount of the *cis*-isomer decreased, and *p*-bis(trimethylsilyl)benzene appeared. After 24 h the *cis*-isomer had virtually disappeared, while the concentration of the aromatic compound continued to increase. Still later, the residual *trans*-isomer was found to be slowly disappearing. Thus it appears that in the reaction of benzene with lithium and chlorotrimethylsilane, both the *cis*- and the *trans*-isomer of 3,6-bis(trimethylsilyl)cyclohexa-1,4-diene are formed initially, but the *cis*- (and to a lesser extent the *trans*-) isomer is subsequently converted into the aromatic compound. Thus if our tentative stereochemical assignments are correct, the 3,6-bis(trimethylsilyl)cyclohexa-1,4-diene isomer isolated by Weyenberg and Toporcer<sup>3</sup> must have been the *trans*-compound.

#### EXPERIMENTAL

<sup>1</sup>H N.m.r. spectra were recorded for solutions in deuteriochloroform [CHCl<sub>3</sub> (τ 2.73) as internal standard] with a Varian A60 spectrometer. I.r. spectra were recorded for liquid films on a Perkin-Elmer 257 grating spectrometer. Analytical and preparative g.l.c. were carried out on a Pye 104, model 64 chromatograph, with SE30, Ucon Oil, or ββ'-oxydipropionitrile (ODPN) columns. Peak area ratios (estimated by the triangulation approximation) have not been corrected for relative detector response. Pre-

<sup>13</sup> H. M. Frey, A. Krantz, and I. D. R. Stevens, *J. Chem. Soc. (A)*, 1969, 1734.

<sup>14</sup> R. G. Harvey, D. F. Lindow, and P. W. Rabideau, *J. Amer. Chem. Soc.*, 1972, **94**, 5412.

<sup>15</sup> L. Benati, M. Tiecco, A. Tundo, and F. Taddei, *J. Chem. Soc. (B)*, 1970, 1443.

<sup>16</sup> D. H. Hey, M. J. Perkins, and G. H. Williams, *J. Chem. Soc.*, 1965, 110.

<sup>11</sup> See, for example, J.-F. Sauvage, R. H. Baker, and A. S. Hussey, *J. Amer. Chem. Soc.*, 1960, **82**, 6090; P. N. Rylander, 'Catalytic Hydrogenation over Platinum Metals,' Academic Press, New York, 1967, p. 81 *et seq.*

<sup>12</sup> L. J. Durham, J. Studebaker, and M. J. Perkins, *Chem. Comm.*, 1965, 456; D. J. Atkinson and M. J. Perkins, *Tetrahedron Letters*, 1969, 2335.

viously reported organosilicon compounds were prepared by published methods, except for 2,6-bis(trimethylsilyl)-toluene, which we made *via* the Grignard route described here rather than the Wurtz route.<sup>17</sup>

**2,6-Bis(trimethylsilyl)toluene.**—To magnesium turnings (23 g, 0.96 g atom), chlorotrimethylsilane (120 g, 1.1 mol), tetrahydrofuran (250 ml), and toluene (150 ml), 2,6-dichlorotoluene (70 g, 0.44 mol) was added at such a rate as to maintain steady reflux. The resulting white slurry was refluxed for 7 h, during which time the temperature of the mixture rose from 70 to 90°. Hydrolysis (ammonium chloride-ice), extraction with ether, drying (MgSO<sub>4</sub>) of the combined extracts, and fractionation, gave 2,6-bis(trimethylsilyl)toluene (68 g, 66%); b.p. 58° at 0.1 mmHg,  $n_D^{25}$  1.5088 (lit.,<sup>17</sup> b.p. 125–126° at 9 mmHg,  $n_D^{20}$  1.5102) (Found: C, 65.7; H, 10.4. Calc. for C<sub>13</sub>H<sub>24</sub>Si<sub>2</sub>: C, 66.0; H, 10.2%).

**Cyclohex-2-enyltrimethylsilane.**—To magnesium turnings (5.2 g, 0.22 g atom), chlorotrimethylsilane (50 g, 0.46 mol), and tetrahydrofuran (150 ml), 3-bromocyclohexene (34 g, 0.21 mol) was added at such a rate as to maintain steady reflux. The resulting white slurry was refluxed for 4 h, and work-up as above gave cyclohex-2-enyltrimethylsilane (25 g, 50%), b.p. 45° at 5 mmHg,  $n_D^{25}$  1.4593 (Found: C, 69.95; H, 11.7. C<sub>9</sub>H<sub>18</sub>Si requires C, 70.0; H, 11.75%).

**Electrochemical Reduction of Arylsilicon Compounds.—General method.** All reactions were carried out in a three-necked flask (1 l) fitted with magnetic stirrer, cold-finger condenser, thermometer, and two platinum-gauze electrodes (20 × 20 mm). This is essentially the 'undivided electrolysis cell' described by Benkeser *et al.*<sup>6</sup> The apparatus was assembled hot, flushed with nitrogen, and charged with anhydrous lithium chloride (*ca.* 10 g) and the arylsilicon compound (*ca.* 0.02 mol), and methylamine (*ca.* 300 ml) was then condensed in. The electrolysis was carried out under nitrogen, without cooling for reactions at -5°, but with intermittent cooling in an ethanol-solid carbon dioxide bath for reactions at lower temperatures. A variable transformer and rectifier system was used for the electrolyses, and *ca.* 500,000 C mol<sup>-1</sup> were passed (0.5–1.5 A at 85–95 V). (A transient colour at the cathode was noted, ranging from green-yellow to a deep blue in the various electrolyses, and was especially marked in the electrolyses at the lower temperatures. In all cases in which such colour was noted, it became a deep blue towards the end of the reduction.) The methylamine was evaporated off, and the residue was 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<sub>4</sub>) and fractionated to give the products as colourless liquids. The following electrolyses were carried out by this method.

**Trimethyl(phenyl)silane.** Electrolysis (2 A for 3.5 h at -5°) of trimethyl(phenyl)silane (7.5 g, 0.05 mol) and lithium chloride (17 g) in methylamine (500 ml) gave cyclohexa-2,5-dienyltrimethylsilane (6.3 g, 84%), b.p. 65° at 20 mmHg (lit.,<sup>1</sup> 168–169°);  $\nu_{\max}$  1670w, 1623w, and 1100s cm<sup>-1</sup>;  $\tau$  4.4 (4H, m), 7.3 (2H, m), 7.8 (1H, m), and 9.98 (9H, s) [lit.,<sup>1</sup> 4.4 (4H, m), 7.26 (2H, m), 7.73 (1H, m), and 9.87 (9H, s)]. G.l.c. (ODPN) showed the presence of cyclohexa-1,4-dienyltrimethylsilane<sup>18</sup> (3%), cyclohex-3-enyltrimethylsilane<sup>18</sup> (3%), and traces of trimethyl(phenyl)silane and cyclohex-2-enyltrimethylsilane.

<sup>17</sup> H. Hopff, J. M. Deuber, P. Gallegra, and A. Said, *Helv. Chim. Acta*, 1971, **54**, 117.

**1,3-Bis(trimethylsilyl)benzene.** Electrolysis (0.6 A for 4 h at -50°) of 1,3-bis(trimethylsilyl)benzene (3.7 g, 0.017 mol) and lithium chloride (6 g) in methylamine (300 ml) gave 1,3-bis(trimethylsilyl)cyclohexa-1,4-diene (2.75 g, 75%), b.p. 58–59° at 0.9 mmHg,  $n_D^{25}$  1.4718 (Found: C, 64.4; H, 11.0. C<sub>12</sub>H<sub>24</sub>Si<sub>2</sub> requires C, 64.2; H, 10.8%);  $\nu_{\max}$  1658w, 1600m, and 1097s cm<sup>-1</sup>;  $\tau$  4.0 (1H, br m), 4.3–4.4 (2H, br m), 7.3–7.4 (2H, br m), 7.6–7.7 (1H, br m), and 9.95 and 9.98 (18H, two s). G.l.c. (Ucon oil) showed the presence of an unidentified compound (*ca.* 8%) and 1,5-bis(trimethylsilyl)cyclohexa-1,4-diene<sup>18</sup> (*ca.* 1%).

**1,2-Bis(trimethylsilyl)benzene.** Electrolysis (1.2 A for 2.5 h at -50°) of 1,2-bis(trimethylsilyl)benzene (4.5 g, 0.02 mol) and lithium chloride (10 g) in methylamine (300 ml) gave a fraction of b.p. 55–56° at 0.65 mmHg (3.4 g, 75%). G.l.c. (Ucon oil) showed the presence of four components in relative yields of 70, 23, 6, and 1%. Preparative g.l.c. (Ucon oil) gave the three major components as colourless liquids. The first two were, respectively, (i) 1,6-bis(trimethylsilyl)cyclohexa-1,4-diene (for analytical and spectroscopic data see Part II<sup>18</sup>) and (ii) 3,4-bis(trimethylsilyl)cyclohexene,  $n_D^{25}$  1.4737 (Found: C, 63.6; H, 11.5. C<sub>12</sub>H<sub>26</sub>Si<sub>2</sub> requires C, 63.6; H, 11.6%);  $\nu_{\max}$  1645w cm<sup>-1</sup>;  $\tau$  4.3 (2H, m), 8.1 (4H, br m), 8.5 (1H, br m), 8.9 (1H, br m), and 9.95 and 10.00 (18H, two s). Only a small amount (*ca.* 5 mg) of the third component was isolated; its spectra [ $\nu_{\max}$  1645w cm<sup>-1</sup>;  $\tau$  9.95 and 9.98 (two s)] suggested that it was either 4,5-bis(trimethylsilyl)cyclohexene or the geometric isomer of the isolated 3,4-bis(trimethylsilyl)cyclohexene.

**1,4-Bis(trimethylsilyl)benzene.** Electrolysis (1.3 A for 1.5 h at -5°) of 1,4-bis(trimethylsilyl)benzene (3.0 g, 0.014 mol) and lithium chloride (10 g) in methylamine (300 ml) gave, after evaporation of the ethereal extract, an involatile (b.p. 60° at 80 mmHg), colourless liquid (2.8 g, 93%). G.l.c. (Ucon oil and SE30) showed the presence of three components in relative yields of 20, 2, and 78%, respectively. The first was *trans*-3,6-bis(trimethylsilyl)cyclohexa-1,4-diene (the compound also prepared by the method of Weyenberg and Toporcer<sup>3</sup>) [ $\tau$  4.54 (4H, m), 7.72 (2H, m), and 9.99 (18H, s)]. Preparative g.l.c. (SE30) gave the third component as a colourless liquid,  $n_D^{25}$  1.4817, which was considered to be *cis*-3,6-bis(trimethylsilyl)cyclohexa-1,4-diene (Found: C, 65.0; H, 11.2. C<sub>12</sub>H<sub>24</sub>Si<sub>2</sub> requires C, 64.2; H, 10.8%);  $\nu_{\max}$  1690w, 1615m, and 1125s cm<sup>-1</sup>;  $\tau$  4.53 (4H, m), 7.74 (2H, m), and 9.98 (18H, s). On exposure to air crystals of 1,4-bis(trimethylsilyl)benzene rapidly separated; physical measurements were therefore carried out where possible under nitrogen with the minimum delay. G.l.c. analysis of the ethereal extract from the electrolysis (0.4 A for 2 h at -50°) of 1,4-bis(trimethylsilyl)benzene (1.0 g, 0.0045 mol) and lithium chloride (10 g) in methylamine (300 ml) showed the presence of the *trans*- and *cis*-compounds in the ratio 15 : 85. The reduction was incomplete, and 25% of the starting material remained. The *trans*- and *cis*-compounds had relative retention times of 0.70 : 1 on Ucon oil, and 0.77 : 1 on SE30.

**Trimethyl-*p*-tolylsilane.** Electrolysis (1.5 A for 3 h at -5°) of trimethyl-*p*-tolylsilane (5.0 g, 0.03 mol) and lithium chloride (10 g) in methylamine (300 ml) gave a fraction of b.p. 68–72° at 12 mmHg (3.7 g, 75%),  $n_D^{25}$  1.4686. G.l.c. analysis (SE30) showed the presence of four components, in

<sup>18</sup> C. Eaborn, R. A. Jackson, and R. Pearce, *J.C.S. Perkin I*, in the press.

relative yields *ca.* 26 : 20 : 27 : 27, which were separated by preparative g.l.c. (SE30), and shown, respectively, to be (i) 4-methylcyclohex-3-enyltrimethylsilane; (ii) 4-methylcyclohexa-1,4-dienyltrimethylsilane (for physical constants and spectroscopic data for both these compounds see Part II<sup>19</sup>); (iii) *trans*-6-methyl-3-trimethylsilylcyclohexa-1,4-diene,  $n_D^{25}$  1.4688 (Found: C, 72.2; H, 10.9.  $C_{10}H_{18}Si$  requires C, 72.2; H, 10.9%);  $\nu_{max}$  1662w, 1615m, and 1100s  $cm^{-1}$ ;  $\tau$  4.2—4.7 (4H, br m), 7.2 (1H, br m), 7.7 (1H, br m), 8.90 (3H, d,  $J$  6 Hz), and 9.93 (9H, s); and (iv) *cis*-6-methyl-3-trimethylsilylcyclohexa-1,4-diene,  $n_D^{25}$  1.4730 (Found: C, 72.6; H, 11.0.  $C_{10}H_{18}Si$  requires C, 72.2; H, 10.9%);  $\nu_{max}$  1670w, 1630m, and 1100s  $cm^{-1}$ ;  $\tau$  4.4 (4H, m), 7.2 (1H, br m), 7.78 (1H, poorly resolved d of t,  $J_t$  2—3,  $J_d$  7—8 Hz), 8.95 (3H, d,  $J$  7 Hz), and 9.98 (9H, s). Electrolysis (at  $-50^\circ$ ) gave the same four compounds in relative yields 6 : 56 : 9 : 29, respectively. G.l.c. analysis (SE30) of the ethereal extract from the electrolysis (at  $-5^\circ$ ) of pure *cis*-6-methyl-3-trimethylsilylcyclohexa-1,4-diene showed that isomerisation to the *trans*-material did not take place. The *trans*- and *cis*-compounds had relative retention times of 0.83 : 1.00 on Ucon oil and 0.87 : 1.00 on SE30.

*Trimethyl-m-tolylsilane.* Electrolysis (2 A for 6.3 h at  $-5^\circ$ ) of trimethyl-*m*-tolylsilane (12.0 g, 0.073 mol) and lithium chloride (12 g) in methylamine (400 ml) gave 3-methylcyclohexa-2,5-dienyltrimethylsilane (9.0 g, 75%), b.p. 69—70° at 14 mmHg,  $n_D^{25}$  1.4748 (Found: C, 72.8; H, 10.95.  $C_{10}H_{18}Si$  requires C, 72.2; H, 10.9%);  $\nu_{max}$  1680w, 1635w, and 1100m  $cm^{-1}$ ;  $\tau$  4.4 (2H, m), 4.65 (1H, m), 7.32 (1H, m), 7.45 (1H, m), 7.7—7.9 (1H, br m), 8.33 (3H, m), and 10.02 (9H, s).

*Pentamethyl(phenyl)disilane.* Electrolysis (1.2 A for 3.5 h at  $-5^\circ$ ) of pentamethyl(phenyl)disilane (5.0 g, 0.023 mol) and lithium chloride (10 g) in methylamine (300 ml) gave cyclohexa-2,5-dienylpentamethyldisilane (3.8 g, 76%), b.p. 78—79° at 3.5 mmHg,  $n_D^{25}$  1.4949 (Found: C, 62.6; H, 10.6.  $C_{11}H_{22}Si_2$  requires C, 62.8; H, 10.5%);  $\nu_{max}$  1665w, 1620w, and 1093s  $cm^{-1}$ ;  $\tau$  4.4 (4H, m), 7.2—7.3 (2H, br m), 7.5—7.7 (1H, br m), and 9.87 and 9.92 (15H, two s).

*Triethyl(phenyl)germane.* Electrolysis (0.6 A for 2.5 h at  $-50^\circ$ ) of triethyl(phenyl)germane (2.86 g, 0.012 mol) and lithium chloride (6 g) in methylamine (300 ml) gave cyclohexa-2,5-dienyltriethylgermane (2.3 g, 80%), b.p. 67—68° at 0.7 mmHg,  $n_D^{25}$  1.5031 (Found: C, 60.6; H, 9.3.  $C_{12}H_{22}Ge$  requires C, 60.3; H, 9.3%);  $\nu_{max}$  1665w, 1620w, and 1085s  $cm^{-1}$ ;  $\tau$  4.3—4.5 (4H, br m), 7.3 (3H, m), and 8.9—9.2 (15H, complex m).

*Trimethyl(phenyl)germane.* Electrolysis (0.8 A for 3 h at  $-5^\circ$ ) of trimethyl(phenyl)germane (3.2 g, 0.016 mol) and lithium chloride (10 g) in methylamine (300 ml) gave cyclohexa-2,5-dienyltrimethylgermane (1.5 g, 50%), b.p. 63—64° at 10 mmHg,  $n_D^{25}$  1.4936 (Found: C, 54.9; H, 8.4.  $C_9H_{16}Ge$  requires C, 54.9; H, 8.2%);  $\nu_{max}$  1670m, 1625m, and 1090s  $cm^{-1}$ ;  $\tau$  4.4 (4H, m), 7.3 (2H, m), 7.6 (1H, m), and 9.83 (9H, m); see also ref. 19.

*Trimethyl(phenyl)tin.* When electrolysis (0.8 A for 3 h at  $-40^\circ$ ) was carried out with trimethyl(phenyl)tin (5.2 g, 0.022 mol) and lithium chloride (10 g) in methylamine (300 ml), a blue-black 'growth' formed at the cathode, and slowly dispersed when the current was switched off. During the work-up white crystals were deposited from the ethereal solution (presumably trimethyltin hydroxide), and

g.l.c. analysis (Ucon oil) showed the presence of cyclohexa-1,4-diene as a major product.

*1,5-Bis(trimethylsilyl)cyclohexa-1,4-diene.* G.l.c. analysis (Ucon oil) of the ethereal extract from the electrolysis (0.7 A for 4.5 h at  $-5^\circ$ ) of 1,5-bis(trimethylsilyl)cyclohexa-1,4-diene (0.2 g, 0.0009 mol) and lithium chloride (5 g) in methylamine (200 ml) showed the presence of *cis*- and *trans*-1,3-bis(trimethylsilyl)cyclohexane<sup>18,20</sup> in the ratio 1 : 9, along with *ca.* 10% of an unidentified compound [possibly 1,5-bis(trimethylsilyl)cyclohexene]. Reduction was incomplete, and the yield of the fully saturated products was *ca.* 60% with respect to the total amount of the products and starting material recovered.

*Cyclohexa-1,4-dienyltrimethylsilane.* G.l.c. analysis (ODPN) of the ethereal extract from the electrolysis (1 A for 3.5 h at  $-5^\circ$ ) of cyclohexa-1,4-dienyltrimethylsilane (1.3 g, 0.0085 mol) and lithium chloride (10 g) in methylamine (300 ml) showed that cyclohex-3-enyltrimethylsilane (42% with respect to the total amount of product and unchanged starting material) was present. Reduction was incomplete, the only other component being starting material.

*Reaction of Benzene with Lithium and Chlorotrimethylsilane in Tetrahydrofuran.*—A mixture of lithium sand (0.775 g, 0.112 g atom), benzene (2.89 g, 0.037 mol), chlorotrimethylsilane (8.14 g, 0.074 mol), and tetrahydrofuran (75 ml) was stirred under argon at 0°. Samples were withdrawn at intervals for analysis by g.l.c. (SE30). The formation of *cis*- and *trans*-3,6-bis(trimethylsilyl)cyclohexa-1,4-diene was observed, the reaction being complete after *ca.* 5 h, with a *cis* : *trans* ratio of 25 : 75. Subsequently 1,4-bis(trimethylsilyl)benzene was detected, the quantity increasing with time with a corresponding loss of the cyclohexadienes. After 24 h the *cis*-isomer had been consumed and continued stirring at 0° resulted in slower loss of the *trans*-isomer.

*Hydrogenation of cis- and trans-6-Methyl-3-trimethylsilylcyclohexa-1,4-diene.*—Hydrogen was bubbled slowly through a solution of *trans*-6-methyl-3-trimethylsilylcyclohexa-1,4-diene (125 mg) in ethanol (30 ml) containing Adams catalyst (*ca.* 0.05 g). Monitoring by g.l.c. showed that the reduction was slow at room temperature, but when the flask was placed in an oil-bath at 70°, the diene was completely consumed in 7 h. Evaporation of the solvent and preparative g.l.c. (Ucon oil) of the residue gave a colourless liquid (50 mg); analytical g.l.c. indicated that two components were present;  $\nu_{max}$  1675w, 1640w, and 1625w  $cm^{-1}$ ;  $\tau$  4.0, 4.4, 9.05 (d,  $J$  7 Hz), 9.98, and 10.03. The presence of the two trimethylsilyl proton resonances (of unequal intensity) in the n.m.r. spectrum, along with the i.r. data, indicates that the major component was trimethyl-(4-methylcyclohex-1-enyl)silane, with trimethyl-(4-methylcyclohex-2-enyl)silane as the minor component.

Under similar conditions, the *cis*-isomer (90 mg) was completely consumed within 2 h at room temperature; the formation and disappearance of an intermediate (presumably the partially hydrogenated product) was observed. Evaporation of the solvent and preparative g.l.c. (Ucon oil) of the residue gave a colourless liquid (30 mg). The i.r. spectrum showed only very weak bands attributable to unsaturation, indicating that the predominant product was *cis*-trimethyl-(4-methylcyclohexyl)silane.

*Hydrogenation of cis- and trans-3,6-Bis(trimethylsilyl)cyclohexa-1,4-diene.*—Hydrogenation in the presence of Adams catalyst (*ca.* 0.1 g) of the crude product from the

<sup>19</sup> S. W. Bennett, C. Eaborn, R. A. Jackson, and R. Pearce, *J. Organometallic Chem.*, 1971, **28**, 59.

<sup>20</sup> C. Eaborn, R. A. Jackson, and R. Pearce, *J.C.S. Perkin I*, in the press.

electrochemical reduction of 1,4-bis(trimethylsilyl)benzene (*ca.* 1 g) in ethanol (30 ml) was monitored by g.l.c. (Ucon oil and SE30). At ambient temperature the reaction was very slow, but when the mixture was warmed at 70°, the *cis*-isomer was consumed within 12 h, whilst the *trans*-isomer was unaffected. The formation of one major product, several minor products, and 1,4-bis(trimethylsilyl)benzene was observed. Evaporation of the solvent followed by preparative g.l.c. (SE30) gave the major product, 3,6-

*bis(trimethylsilyl)cyclohexene* as a colourless liquid,  $n_D^{25}$  1.4780 (Found: C, 63.35; H, 11.3.  $C_{12}H_{26}Si_2$  requires C, 63.6; H, 11.6%);  $\nu_{max}$  1635  $cm^{-1}$ ;  $\tau$  ( $CS_2$ ) 4.4 (2H, m), 8.3 (6H, m), and 10.00 (18H, s).

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