Reduction of Aryltrimethylsilanes as a Synthetic Method. Part III.[1] Lithium in Ethylamine (Benkeser Reduction)

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Reduction of five aryltrimethylsilanes and one cyclohexenyltrimethylsilane with lithium in ethylamine gives cyclohexanes in every case. Cleavage of one carbon–silicon bond occurs in 1,3-bis(trimethylsilyl)benzene and 1,3,5-tris(trimethylsilyl)benzene. The stereochemistry of the disubstituted cyclohexanes has been assigned.

LITHIUM in low molecular weight amines (Benkeser reduction:[2] for a recent review see ref. 3) is a more powerful, but sometimes less selective, reducing agent for aromatic and olefinic compounds than is sodium or lithium in liquid ammonia (Birch reduction), partly because of the higher temperatures which can be employed in the lithium–amine system. We have used lithium in ethylamine to reduce a number of aromatic and olefinic trimethylsilanes to saturated derivatives.

RESULTS AND DISCUSSION

In general, aryltrimethylsilanes are reduced electrolytically to the corresponding cyclohexa-1,4-dienes, the position of reduction being determined by the electron-density distribution in the intermediate anion radical and by steric influences.[4] The Birch reduction is more powerful. In addition to cyclohexa-1,4-dienes, products of further reduction are obtained when the expected primary reduction products contain vinylic trimethylsilyl groups: in these cases the vinylic double bond is reduced. Allylic trimethylsilyl groups undergo silicon–carbon bond cleavage.[1]
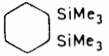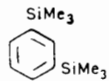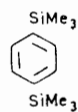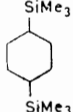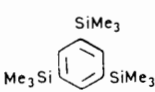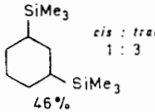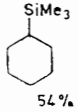
We have investigated the use of lithium in ethylamine as a more powerful reducing agent on a number of aryltrimethylsilanes and one cyclohexenyltrimethylsilane (Table 1). In each case the product is fully saturated.

Trimethyl(phenyl)silane gives cyclohexyltrimethylsilane in poor yield, but o-bis(trimethylsilyl)benzene gives a good yield of the expected cyclohexane derivative. m-Bis(trimethylsilyl)benzene and 1,3,5-tris(trimethylsilyl)benzene undergo loss of one of the trimethylsilyl groups (as in the Birch reduction), but p-bis(trimethylsilyl)benzene gives 20% of the saturated disubstituted compound.

Stereochemistry of the Reactions.—It is convenient to consider the stereochemistry of these reductions along with the two examples of fully reduced compounds[1] which are produced by the Birch reduction of (I) and (II) at −30°. With the exception of o-bis(trimethylsilyl)-benzene, all the compounds studied gave a preponderance of the thermodynamically less stab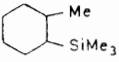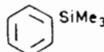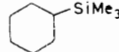le isomer. Stereoselectivity is better for the lithium–ethylamine method, in spite of the higher temperatures employed, and still better selectivity is observed in the electro-

chemical reduction of 1,5-bis(trimethylsilyl)cyclohexa-1,4-diene.[4] A rationalisation for the preferential form-

TABLE 1

Lithium–ethylamine reductions

Starting material	Products, with relative yields	% Isolated
1,2-bis(SiMe₃)benzene	1,2-bis(SiMe₃)cyclohexane, cis : trans 1 : 1	73
1,3-bis(SiMe₃)benzene	SiMe₃ cyclohexane	75
1,4-bis(SiMe₃)benzene	1,4-bis(SiMe₃)cyclohexane, cis- (?)	20
1,3,5-tris(SiMe₃)benzene	1,3-bis(SiMe₃)cyclohexane (cis : trans 1 : 3) 46% + SiMe₃ cyclohexane 54%	61
Me, SiMe₃ cyclohexene	Me, SiMe₃ cyclohexane, cis : trans 86 : 14	a
SiMe₃ benzene	SiMe₃ cyclohexane	b 15

a Detected and estimated by g.l.c. b A higher b.p. fraction containing Si–O linkages was also obtained.

ation of the less stable isomer has been proposed for similar systems on the basis of the steric requirement for

1,3-bis(Me₃Si)benzene (I) + Li-NH₃-EtOH, −30° → 1,3-bis(SiMe₃)cyclohexane, cis : trans 43 : 57

Me, SiMe₃ cyclohexene (II) + Li-NH₃-EtOH, −30° → Me, SiMe₃ cyclohexane, cis : trans 60 : 40
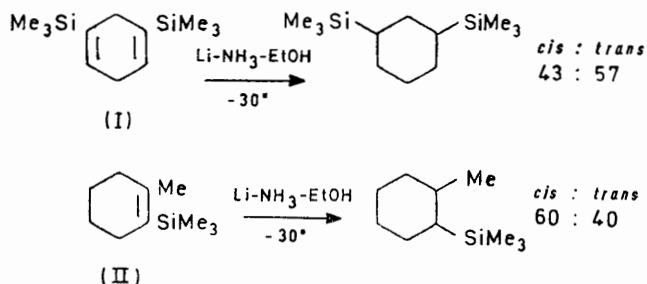
[1] Part II, C. Eaborn, R. A. Jackson, and R. Pearce, preceding paper.
[2] R. A. Benkeser, R. E. Robinson, D. M. Sauve, and O. H. Thomas, *J. Amer. Chem. Soc.*, 1955, **77**, 3230.
[3] E. M. Kaiser, *Synthesis*, 1972, 391; see also H. Kwart and R. A. Conley, *J. Org. Chem.*, 1973, **38**, 2011.
[4] C. Eaborn, R. A. Jackson, and R. Pearce, *J.C.S. Perkin I*, 1974, 2055.

protonation of the intermediate anion.[5] Approach of the solvent molecule will be easiest along an equatorial direction, leadin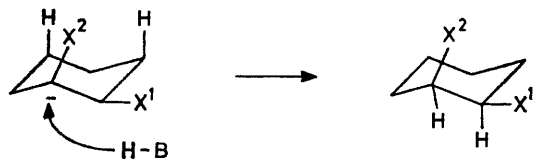g to an axial product, whereas approach in the axial direction will be hindered by axial hydrogen atoms or other groups.

o-Bis(trimethylsilyl)benzene gives a roughly 50 : 50 mixture of the two isomers. The reason for this is not clear, but a clue may be provided by the fact that electrochemical reduction of this compound gives as major products (III) and (IV).[4] If the Benkeser reduction involves sequentially (III) and (IV), the stereochemistry
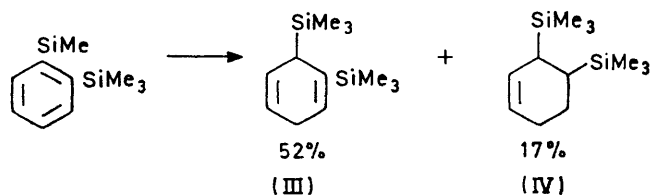
of the product mixture will be defined during this stage of the reaction. Since cyclohexenes are 'flatter' than cyclohexanes, the two directions of approach will be more nearly equally favourable, with a consequent approach to a 50 : 50 cis : trans product mixture.

Assignment of Stereochemistry.—The assignment of stereochemistry to the geometrical isomers of 1,2- and 1,3-bis(trimethylsilyl)cyclohexane and 1-methyl-2-trimethylsilylcyclohexane was based on their refractive indices, g.l.c. retention times, and n.m.r. data.

The modified Auwers–Skita rule states that for cyclic stereoisomers in which the substituents are bound to configurationally identical ring systems, the isomer with the higher density and the higher refractive index is that which has the higher heat content.[6] On this basis, we may assign the stereochemistry of the six compounds listed in Table 2.

A previous re-statement of the Auwers–Skita rule had included b.p.[7] (higher b.p. associated with the less stable isomer), but there are objections to the inclusion of b.p. in the rule.[6] We have been unable to separate our isomer mixtures by distillation, but it is known that for compounds which have only subtle differences in structure, relative retention times on non-polar g.l.c. columns normally increase with increasing b.p. of the compound. The relative retention times of the three pairs of compounds listed in the Table are in accordance with the assignments of stereochemistry based on refractive index.

The n.m.r. spectra of the compounds support the

stereochemical assignments in a number of ways. The spectra of compounds (VI)—(VIII) were essentially temperature-independent down to —80°, but at ca. —70°

TABLE 2

Properties of some disubstituted cyclohexanes

Compound	Stereo-isomer	Number	Relative retention time (SE30 column)	n_D^{25}
SiMe₃ / SiMe₃	cis	(V)	1·00	1·4747
SiMe₃ / SiMe₃	trans	(VI)	0·80	1·4672
SiMe₃ / SiMe₃	trans	(VII)	1·00	1·4580
SiMe₃ / SiMe₃	cis	(VIII)	0·90	1·4550
Me / SiMe₃	cis	(IX)	1·00	1·4552
Me / SiMe₃	trans	(X)	0·92	1·4531

the single trimethylsilyl resonance of compound (V) split into two (separation at —80°, 5·5 Hz). At this low temperature exchange between the *ax,eq* and *eq,ax* conformations is presumably slow enough for the two types of group to give separate absorptions: for the interchange of the two conformations, the two bulky trimethylsilyl groups must pass each other in the 1,2-compounds, though not in the 1,3-compounds. Variable temperature studies on the analogous cis-1,2-di-t-butylcyclohexane [8] have been interpreted as showing the presence of a considerable amount of the twist form at equilibrium, with hindered pseudorotation in the twist form. Catalin models show that similar hindrance to pseudorotation in (V) is also possible, though the effect will be less pronounced. Although the trimethylsilyl group is spatially larger than the t-butyl group, the fact that the C–Si bond is longer than the C–C bond will result in considerably less repulsion between one trimethylsilyl group and either another one or the *syn*-axial protons. Thus appreciable quantities of the twist form at equilibrium are not to be expected.

Two less certain n.m.r. indications of stereochemistry are as follows. (i) Isomer (IX) showed two methyl resonances, whereas (X) showed only one signal. By analogy with cis- and trans-1,2- and 1,4-dimethylcyclohexanes,[9] which show two signals when an axial methyl group is present but only one when both methyl groups are equatorial, we infer that (IX) and (X) are respectively the cis- and trans-isomers of 1-methyl-2-trimethylsilylcyclohexane. However, both cis- and trans-1,3-dimethyl-

[5] H. Smith, 'Organic Reactions in Liquid Ammonia,' (vol. 1, part II of 'Chemistry in Non-aqueous Ionising Solvents), Interscience, New York, 1963.

[6] H. van Bekkum, A. van Veen, P. E. Verkade, and B. M. Wepster, *Rec. Trav. chim.*, 1961, **80**, 1310.

[7] N. L. Allinger, *Experientia*, 1954, **10**, 328.

[8] H. Kessler, V. Gusowski, and M. Hanack, *Tetrahedron Letters*, 1968, 4665.

[9] N. Muller and W. C. Tosch, *J. Chem. Phys.*, 1962, **37**, 1167, and references therein.

cyclohexane show two methyl resonances. (ii) The n.m.r. spectra of the 1,2-cis- and the 1,3-trans-isomers showed considerably narrower methylene resonances than the corresponding 1,2-trans- and 1,3-cis-isomers. In cis-1,2-bis(trimethylsilyl)cyclohexane (V), the peaks extended from τ 7·8 to 9·1, overlapping with the methine resonances at τ 9·1. The appearance of a relatively narrow region of ring proton resonances can in some cases [9] imply a rapid ring inversion (with a consequent averaging of chemical shifts). There will be rapid inter-conversion between the ax,eq and eq,ax conformers in the 1,2-cis- and 1,3-trans-isomers to give a time-averaged spectrum, whereas the 1,2-trans- and 1,3-cis-isomers will behave as conformationally rigid (eq,eq) molecules. On this basis, the single isomer of 1,4-bis(trimethylsilyl)-cyclohexane is tentatively assigned the cis-structure.

EXPERIMENTAL

G.l.c. and spectroscopic measurements were carried out as described in Part I.[4]

Reduction of Arylsilicon Compounds with Lithium in Ethylamine.—All reactions were carried out in a 100 ml two-necked flask fitted with magnetic stirrer and cold-finger con-denser (ethanol–solid CO_2). The apparatus was assembled hot, flushed with nitrogen, and charged with the arylsilicon compound (ca. 0·01 mol) and ethylamine (ca. 75 ml). Lithium strips (in excess) were added and the solution was stirred until a deep blue colouration persisted. (The solu-tions generally became coloured shortly after the addition of the lithium; deep orange, yellow, and green colourations were obtained in different reactions before the onset of the blue colouration.) The excess of lithium was destroyed with ammonium chloride, and the ethylamine was evapor-ated off. Work-up as before [1] gave the products as colour-less liquids. The following reductions were carried out by this method.

1,2-Bis(trimethylsilyl)benzene. 1,2-Bis(trimethylsilyl)-benzene (1·9 g) and lithium (1 g) gave a fraction of b.p. 66—67° at 1·5 mmHg (1·4 g, 73%). G.l.c. (Ucon oil and SE30) showed the presence of two compounds in the ratio 1 : 1, with ca. 4% of an unidentified product. Preparative g.l.c. (Ucon oil) gave the two major components as colourless liquids. One was trans-1,2-bis(trimethylsilyl)cyclohexane, n_D^{25} 1·4672 (Found: C, 63·0; H, 12·55. $C_{12}H_{28}Si_2$ requires C, 63·1; H, 12·35%); τ 8·2—8·6br (8H, m), 9·8 (2H, m), and 9·88 (18H, s). The other was cis-1,2-bis(trimethylsilyl)-cyclohexane, n_D^{25} 1·4747 (Found: C, 63·3; H, 12·45%); τ 8·4 (8H, m), 8·9 (2H, m), and 9·88 (18H, s). Relative reten-tion times of the trans- and cis-isomers were 0·72 : 1 (on Ucon oil) and 0·80 : 1 (on SE30). The n.m.r. spectrum (in CS_2 solution) of the trans-isomer was essentially invariant from 25 to —80°; the corresponding spectrum of the cis-isomer at —80° showed the signal at 9·88 had split into two (separation 5·5 Hz) at τ 9·93 and 10·02₅; the low-field portion of the spectrum was considerably broadened, with absorption from τ 7·9 to 9·2. The temperature of coales-cence of the high-field pair was ca. —70°.

1,3,5-Tris(trimethylsilyl)benzene. 1,3,5-Tris(trimethyl-silyl)benzene (2·6 g) and lithium gave cyclohexyltrimethyl-silane (0·45 g, 33%), b.p. 53° at 10 mmHg, (lit.,[10] 67—69° at 20 mmHg) and a fraction (0·54 g, 28%), b.p. 49—50° at 0·35 mmHg. G.l.c. (Ucon oil) showed the presence of cis- and trans-1,3-bis(trimethylsilyl)cyclohexane in relative yields of 25 and 75%, respectively.

1,4-Bis(trimethylsilyl)benzene. 1,4-Bis(trimethylsilyl)-benzene (5·0 g) and lithium (1·2 g) gave cis(?)-1,4-bis(tri-methylsilyl)cyclohexane (1·0 g, 20%), b.p. 60—63° at 0·8 mmHg, n_D^{25} 1·4591 (Found: C, 63·5; H, 12·2. $C_{12}H_{28}Si_2$ requires C, 63·1; H, 12·35%); τ 8·4—8·5 (8H, m), 9·1—9·2 (2H, m), and 10·0 (18H, s); m/e 228.

1,3-Bis(trimethylsilyl)benzene. 1,3-Bis(trimethylsilyl)-benzene (4·2 g) and lithium gave cyclohexyltrimethylsilane (3·1 g, 75%), b.p. 52—53° at 9 mmHg, (lit.,[10] 67—69° at 20 mmHg).

Trimethyl(phenyl)silane. Trimethyl(phenyl)silane (4·3 g) and lithium (1·3 g) were stirred in ethylamine (75 ml) for 12 h. Lithium (0·3 g) was added and stirring was continued (12 h), but at no time did the solution acquire the characteris-tic deep blue colouration. The lithium was consumed in this time. Work-up gave a fraction (0·63 g, 15%) of b.p. 168—172° which was mainly cyclohexyltrimethylsilane (g.l.c.), and a further fraction (0·3 g), b.p. 55—60° at 2 mmHg. G.l.c. (SE30) showed the presence of cyclohexyl-trimethylsilane and an unidentified compound; the i.r. spectrum showed bands attributable to Si–O–Si or Si–O–C linkages.

Trimethyl-(2-methylcyclohex-1-enyl)silane. G.l.c. (Uconoil) of the ethereal extract of the mixture from reduction of tri-methyl-(2-methylcyclohex-1-enyl)silane [1] (0·9 g) with lithium (0·3 g) showed the presence of trans- and cis-trimethyl-(2-methylcyclohexyl)silane in relative yields of 14 and 86%, respectively.

[10] W. H. F. Sasse and K. O. Wade, Austral. J. Chem., 1966, 19, 1897.