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ADDITION OF IODINE-BASED ELECTROPHILIC REAGENTS TO SOME VINYLSILANES

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Abstract - The addition of some iodine-based electrophilic reagents to the cyclic vinylsilanes (1) and (4,R=Bu^t,R^1=H) and (4,R=H,R^1=OMe) occurs with high regio-and stereo-specificity to give (2,X=OMe,N$_3$ and NCS) and (5,R=Bu^t,R^1=H,X=OMe and N$_3$) and (5,R=H,R^1=OMe,X=OMe). Similar additions to 2-trimethylsilylhept-1-ene (6) are less efficient and occur with lower regioselectivity. Some of the adducts (2) and (5) have been transformed into functionalised organosilanes. Compounds (10,X=OMe,N$_3$, and NCS) and (12)-(15) are thereby obtained.

The literature on reactions of electrophilic reagents with vinylsilanes (αβ-unsaturated silanes) has been well surveyed by Colvin.[1] In many instances overall electrophilic substitution of the silyl group ensues, thereby accounting for the synthetic importance of the process, particularly where a carbocationic reagent is involved. In other cases actual adducts have been isolated.

In this paper we describe an investigation of the addition of iodine-based electrophilic reagents ("IX") to some vinylsilanes,[2] choosing those reagents where the formation of isolable adducts could be expected by analogy with the behaviour of other olefins.[3] We wished to determine the regio- and stereo-chemistry of addition for comparison with the mode of ring opening of the corresponding αβ-epoxysilanes[4] with the intention of improving the understanding of the controlling influence exerted by silicon in such reactions. It was also hoped that further chemical transformations of the "IX" adducts might provide useful routes to functionalised organosilicon compounds.

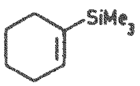
RESULTS

Adducts (2) X=OMe, N$_3$ and NCS were obtained in reasonable yield by addition of the appropriate iodine-based reagents to 1-trimethylsilylcyclohexene (1) as summarised in Table 1. Only in the case of I$_2$-LiOAc as reagent was iododesilylation a significant process. The adducts (2) were identified by a combination of spectroscopic data (see experimental section) and further chemical transformations (see below) especially the elimination of HI on treatment with DBU to give 3-substituted 2-trimethylsilylcyclohexenes. In the ^{1}H n.m.r. spectra, the Me$_3$Si signal for compounds containing the Me$_3$SiC-I system showed a characteristic downfield shift of ca. 0.1 p.p.m. compared to that in non I-containing compounds. For comparison purposes, the reaction of I$_2$-LiSCN with cyclohexene under the conditions used for (1) was carried out giving the iodothiocyanate (3)[5] as main product.

Table 1 Addition of "IX" to 1-trimethylsilylcyclohexene (1)

Reagent	Product, %[a]
I_2/MeOH/sulpholane	(2,X=OMe), 89
I_2/LiN_3/sulpholane/$CHCl_3$	(2,X=N_3), 79
I_2/LiSCN/sulpholane/$CHCl_3$	(2,X=NCS), 64
I_2/LiOAc/sulpholane/$CHCl_3$	1-iodocyclohexene, 70

[a] percentage refers to crude yield of isolated product, substantially one compound by n.m.r.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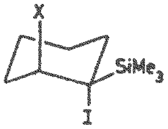
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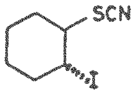
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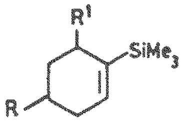
Adducts (5) were also obtained from 4-t-butyl-1-trimethylsilylcyclohexene (4,R=Bu^t,R^1=H) and 3-methoxy-2-trimethylsilylcyclohexene (4,R=H,R^1=OMe) see Table 2.

Table 2 Addition of "IX" to substituted 1-trimethylsilylcyclohexenes (4)

Substrate	Reagent	Product, %[a]
(4,R=Bu^t,R^1=H)	I_2/MeOH/sulpholane	(5,R=Bu^t,R^1=H,X=OMe), 83
(4,R=Bu^t,R^1=H)	I_2/LiN_3/sulpholane/$CHCl_3$	(5,R=Bu^t,R^1=H,X=N_3), 86
(4,R=H,R^1=OMe)	I_2/MeOH/sulpholane	(5,R=H,R^1=OMe,X=OMe), 90

[a] percentage refers to crude yield of isolated product, substantially one compound by n.m.r.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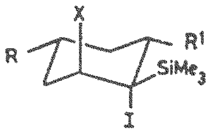

(5)


(6)

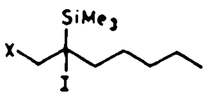
Attempts to obtain adducts from 2-trimethylsilylhept-1-ene (6), Table 3, were less successful than for the cyclic vinyl silanes. In each case products considered to have been derived via 1-iododerivative (8) were obtained in addition to the expected 2-iodo-adducts (7). Thus, for example, heptan-2-one (Table 3, entry 1) had presumably been formed from (8,X=OMe) by β-elimination followed by hydrolysis of the resulting vinyl ether. We also briefly looked at the reaction of I_2-MeOH with α-trimethylsilylstyrene[6] however the main product was acetophenone presumed to have been formed via (9).

Table 3 Addition of "IX" to 2-trimethylsilylhept-1-ene (6)

Reagent	Products, %[a]	β/α ratio[b]
I_2/MeOH/sulpholane	(7,X=OMe),58; heptan-2-one,12	4.8
I_2/LiN_3/sulpholane/$CHCl_3$	(7,X=N_3),24; 2,2-diazido-1-iodoheptane,9	2.7
I_2/LiSCN/sulpholane/$CHCl_3$	(7,X=SCN),48; 2-thiocyanatohept-1-ene, 24	2.0

[a] percentages estimated from n.m.r. spectrum of crude product.

[b] β and α refer respectively to attack by X β and α to Si.



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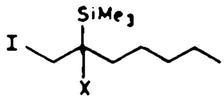

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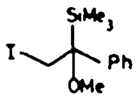
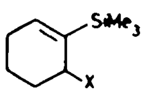


(9)

Having successfully prepared 'IX' adducts from the 1-trimethylsilylcyclohexenes (Tables 1 and 2) we decided to explore briefly their utility as precursors of functionalised organo-silicon compounds by substitution and elimination reactions. Thus the adducts (2) were converted into 3-substituted-2-trimethylsilylcyclohexenes (10) by treatment with DBU in benzene under reflux. In this way the methyl ether (10,X=OMe), the allylic azide (10,X=N$_3$) and the isothiocyanate (10,X=NCS) were prepared, thereby providing chemical evidence for the regio- and stereo-chemistry of the adducts (2). The allylic ethers (11) and (12) were obtained similarly by elimination of HI from their respective precursors (5, R=Bu^t, R'=H, X=OMe) and (5, R=H,R'=X=OMe).



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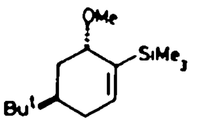

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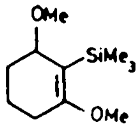
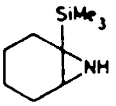


(12)

Reduction of the iodoether (2,X=OMe) with LAH in THF gave a 1:1 mixture of cis- and trans-2-methoxy-1-trimethylsilylcyclohexane presumably by a radical mechanism[7] which would be non-stereospecific. The allylic amine (10,X=NH$_2$) was obtained by reduction of the allylic azide (10,X=N$_3$) by LAH in Et$_2$O. Treatment of the iodoazide (2,X=N$_3$) with LAH in Et$_2$O resulted in reduction-cyclisation to the aziridine (13) which was only obtained as the crude material; no evidence for formation of 2-amino-1-trimethylsilylcyclohexane was obtained, presumably C-I cleavage does not occur prior to azide reduction as in some acyclic cases.[8] The iodoisothiocyanate (2,X=NCS) underwent cyclisation to the thiazoline (14) on treatment with KOH in MeOH, while the allylic isothiocyanate (10,X=NCS) gave the thiocarbamate (10,X=NHCSOMe) under similar conditions. Acidic hydrolysis of the enol ether (12) gave the unsaturated ketone (15).[9]



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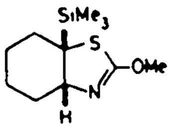

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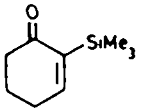
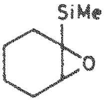


(15)

DISCUSSION

Addition of the various iodine-based reagents to 1-trimethylsilylcyclohexene (1), 4-t-butyl-1-trimethylsilylcyclohexene (4,R=Bu^t,R'=H) and 3-methoxy-2-trimethylsilylcyclohexene (4,R=H,R'=OMe) occurred regiospecifically with the iodo-group attacking α- to silicon. The stereochemical result is that expected for diaxial anti-addition. We consider that the conditions used are such as to favour an ionic mechanism, probably involving an intermediate iodonium ion, rather than a free radical mechanism.[10] Reversible iodonium ion formation involving initial attack from either side is presumed,[11] to account for the formation of adducts (5,R=Bu^t,R'=H) with I cis to Bu^t in the conformationally biased system. There would appear to be two ways of rationalising the regiochemical result. One is to postulate that the transition state for iodonium ion ring opening has sufficiently high S$_N$2 character that the orientation is governed by the steric effect of Me$_3$Si. The other is to propose an S$_N$1 like transition state thereby appealing to the stabilising effect of the C-Si bond on the β-carbonium ion[12] as the regiochemically determining factor. Although Berti et al[13] have argued against the second interpretation, it is the one we favour. In the majority of cases of addition of 'IX' to unsymmetrical alkenes there is a marked tendency, where steric effects are relatively unimportant, for 'Markownikov' orientation to be found with iodine becoming attached to the less substituted carbon.[3] An unsymmetrical transition state for iodonium ion opening, with significant cationic character at the carbon being attacked by the nucleophile, provides an attractive rationalisation. In this connection it is instructive to compare the regioselectivity of addition of IX to (1) with that of acid catalysed ring opening of the epoxide (16),[14] where 'good' nucleophiles attack at the carbon α- to silicon, e.g. the reaction of (16) with HI to give the iodohydrin (2,X=OH). Here, apparently, there is insufficient C-O breaking and structural reorganisation at the transition state for the β-silicon cation stabilising effect to operate. Instead, the α-silicon effect favouring S_N2 attack at the α-carbon dominates. This comparison provides another strand in the argument against the above mentioned steric explanation for the mode of iodonium ion opening.



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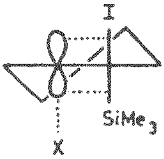

(17)

A number of authors have pointed out that, in the acid catalysed ring opening of αβ-epoxysilanes, the relative orientations of the C-Si and the $C_β$-O bonds deviate markedly from the coplanar arrangement favourable for stabilisation of a developing positive charge by the C-Si bond. It might have been expected that the same would be true for the corresponding iodonium ion but our explanation is not in agreement with that view. Possibly the transition state for iodonium ion opening is looser and less reactant like than that from the protonated epoxide thus allowing sufficient structural reorganisation to occur to permit C-Si hyperconjugation. Formula (17) is an attempt at a crude representation.

It is noteworthy that the I_2/LiCNS product is the isothiocyanate (2, X=-N=C=S) while in the ring opening of the epoxysilane with 'thiocyanic acid' the predominant product is the thiocyanate.[4] A transition state of dominant S_N2 character is expected to favour S-attack, while N-attack involving this ambident nucleophile could be a consequence of increased S_N1 character.

The results in the case of the 1-alkylvinylsilane (6) were disappointing (Table 3). Only in one case, formation of the methoxyiodide (7,X=OMe), was the yield synthetically respectable and the regioselectivity (β/α ratio: 4.8) useful. Clearly the effect of Me_3Si in directing orientation in favour of β-attack, which dominated the cyclohexyl system (1), is insufficiently strong to override completely the normal preference for IX reagents to add to terminal olefins in the 'Markownikov' sense. In contrast, addition of "iodine azide" to 1-trimethyl-silylprop-1-ene, where the two effects operate in concert, occurs with high regio-and stereo-specificity to give 2-azido-1-iodo-1-trimethylsilyl-propane.[8]

EXPERIMENTAL

^1H N.m.r. spectra were recorded on a Perkin-Elmer R14 (100 MHz) or a R32 (90 MHz) instrument for solutions in $CDCl_3$ using $CHCl_3$ as internal standard. P.l.c. was carried out on 20 x 20 cm plates or 100 x 20 cm plates coated with unbaked Kieselgel $HF_{254+366}$ using ether/light petroleum (b.p. 40-60°C) mixtures as eluant.

t-1-Iodo-c-2-methoxy-r-1-trimethylsilylcyclohexane. - Standard procedure for iodine/methanol addition to vinylsilanes. Iodine (15.25 g, 36 mmol) was added to a stirred mixture of anhydrous methanol (50 ml) and anhydrous sulpholane (50 ml) at 0°C.

1-Trimethylsilylcyclohexene (3.85 g, 15 mmol) was added. The mixture was stirred at 18°C for 24 h.* It was poured into distilled water (100 ml) and extracted with ether (3 x 75 ml). The ethereal solution was washed successively with water (50 ml), saturated aqueous sodium bicarbonate (50 ml), water (50 ml) saturated aqueous sodium metabisulphite (2 x 50 ml), water (50 ml) and brine and was dried ($MgSO_4$). Evaporation of the ether at 18°C gave crude t-1-iodo-c-2-methoxy-r-1-trimethylsilylcyclohexane (7.38 g, 89%) as a brown oil. It was purified by p.l.c. using light petroleum-ether (4:1) as eluant to give the *adduct* as a colourless oil. (Found: C, 40.25; H, 7.0. $C_{10}H_{21}OSiI$ requires C, 40.55; H, 7.15%); 0.18 (9H,s,$SiMe_3$), 0.7-2.5 (8H,m), 3.24 (3H,s,OMe), 3.64 (1H,t,*J* 3Hz,2-H), δ_C ($CDCl_3$) 82.2 (d, C-2) 56.0 (q, OCH_3) 52.7 (s, C-1), 31.7 (t), 23.6 (t), 23.0 (t), 19.9 (t), 0.0 (q, TMS), -1.2 (q, $SiMe_3$).

c-2-*Azido*-t-1-*iodo*-r-1-*trimethylsilylcyclohexane*. - standard procedure for iodine/lithium azide addition to vinylsilanes.- Iodine (9.15 g, 36 mmol) was added in small quantities with stirring during 1h to dry sulpholane (50 ml), dry chloroform (50 ml) and lithium azide (2.2 g, 45 mmol) at 0°C. The mixture was stirred at 0°C for 1 h. 1-Trimethylsilylcyclohexene (2.3 g, 15 mmol) was added and the mixture was stirred at 18°C in the dark for 24 h. It was poured into water (200 ml) and the chloroform layer separated. The aqueous layer was extracted with ether (3 x 100 ml). The ethereal extracts were combined with the chloroform solution and washed with water (100 ml), saturated aqueous sodium bicarbonate (100 ml), water (100 ml), saturated aqueous sodium metabisulphite (100 ml), water (100 ml) and brine and were dried ($MgSO_4$). The solvent was removed at 18°C yielding crude c-2-azido-t-1-iodo-r-1-trimethylsilylcyclohexane as a pale brown oil (3.85 g, 79%). Purification by p.l.c. using light petroleum-ether (4:1) as eluant gave the *iodoazide* as a colourless oil. (Found: C, 33.65; H, 5.65; N, 12.75; I, 38.95. $C_9H_{18}N_3SiI$ requires C, 33.45; H, 5.6; N, 13.0; I, 39.25%). δ_H 9.8 (9H,s,$SiMe_3$), 1.5-2.8 (8H,m), 4.06 (1H,brs,2-H).

t-1-*Iodo*-c-2-*isothiocyanato*-r-1-*trimethylsilylcyclohexene*. - standard procedure for iodine/lithium thiocyanate addition to vinylsilanes.- Iodine (9.15 g, 26 mmol) was added in small quantities with stirring during 1 h to dry sulpholane (50 ml), dry chloroform (50 ml) and lithium thiocyanate (2.9 g, 45 mmol) at 0°C. The mixture was stirred at 0°C for 1 h. 1-Trimethylsilylcyclohexene (2.3 g, 15 mmol) was added and the mixture was stirred at 18°C in the dark for 24 h. It was poured into water (200 ml) and the chloroform layer separated. The aqueous layer was extracted with ether (3 x 100 ml). The ethereal extracts were combined with the chloroform solution and washed with water (100 ml), saturated aqueous sodium bicarbonate (100 ml), water (100 ml), saturated aqueous sodium metabisulphite (100 ml), water (100 ml) and brine and were dried ($MgSO_4$). The solvent was removed at 18°C giving crude t-1-iodo-c-2-isothiocyanato-r-1-trimethylsilylcyclohexane as a brown oil (3.25 g, 64 %). Purification by p.l.c. using light petroleum-ether (4:1) as eluant gave the *adduct* as a colourless oil. (Found: C, 36.15; H, 5.4; S, 9.45; N, 4.25; I, 37.15. $C_{10}H_{18}SNSiI$ requires C, 35.4; H, 5.35; S. 9.45; N, 4.15; I, 37.4%). δ_H 0.22 (9H,s,$SiMe_3$), 1.5-2.8 (8H,m), 4.12 (1H,brs,2-H), ν_{max} (film) 2100 (-N=C=S), m/e 339 (M^+), 266 (M- 73, $SiMe_3$), 212 (M-127, I).

Reaction of Cyclohexene with Iodine and Lithium Thiocyanate.- Cyclohexene (0.41 g, 5 mmol) was treated with iodine (3.05 g, 12 mmol) and lithium thiocyanate (0.975 g, 15 mmol) in dry chloroform (25 ml) and dry sulpholane (25 ml) according to the standard procedure. The crude product was obtained as a yellow oil (2.25 g) considered to be mainly *trans*-2-iodo-1-thiocyanatocyclohexane on the basis of: δ_H 1.3-2.65 (8H,m), 3.48 (1H,m,1-H), 4.28 (1H,m,2-H), (lit.[5], δ_H (CCl_4) 3.52 (m), 4.34 (m)), ν_{max} (film) 2150 cm^{-1} (-S-C≡N).

Reaction of 1-Trimethylsilylcyclohexene with Iodine/Lithium Acetate - standard procedure for reactions of iodine/lithium acetate with vinylsilanes.- Iodine (3.05 g, 12 mmol) was added in small quantities during 1 h to a stirred mixture of dry sulpholane (25 ml), dry chloroform (25 ml) and lithium acetate (0.975 g, 15 mmol) at 0°C. The mixture was stirred for 1 h at 0°C. 1-Trimethylsilylcyclohexene (0.77 g, 5 mmol) was added and the mixture stirred at 18°C in the dark for 24 h. Water (75 ml) was added and the chloroform layer separated. The aqueous layer was extracted with ether (3 x 50 ml). The ethereal extracts and the chloroform solution were combined and washed with water (50 ml), saturated aqueous sodium bicarbonate (50 ml), water (50 ml) saturated aqueous sodium metabisulphite (50 ml), water (50 ml) and brine and were dried ($MgSO_4$). The solvent was removed at 18°C giving a brown liquid (0.975 g, 70%) which was identified after distillation as 1-iodocyclohexene, b.p. 48°C at 1 mm Hg (lit.[19], b.p. 53°C at 5 mm Hg). (Found: C, 34.85; H, 4.6; I, 60.35. Calc for C_6H_9I: C, 34.65; H, 4.35; I, 61.0%). δ_H 1.5 - 2.6 (8H,m), 6.25 (1H,brs,2-H).

t-4-*t*-*Butyl*-t-1-*iodo*-c-2-*methoxy*-r-1-*trimethylsilylcyclohexane*. 4-t-Butyl-1-trimethylsilylcyclohexene (1.05 g, 5 mmol) was treated with iodine (3.05 g, 12 mmol) in dry methanol (50 ml) and dry sulpholane (20 ml) by the standard procedure. The crude product was isolated as a pale brown oil (1.52 g, 83%). Purification by p.l.c. using light petroleum-ether (4:1) as eluant gave t-4-*t*-*butyl*-t-1-*iodo*-c-2-*methoxy*-r-*trimethylsilylcyclohexane* as a colourless oil. (Found: C, 46.25; H, 8.3; I, 34.3. $C_{14}H_{29}OSiI$ requires C, 45.65; H, 7.9; I, 34.45%). δ 0.18 (9H,s,$SiMe_3$), 0.88 (9H,s,Bu^t), 1.1-2.1 (7H,m), 3.25 (3H,s,OMe), 3.75 (1H,brs,2-H), m/e 311 (M- 57, CMe_3), 264 (M- 104, CH_2OSiMe_3).

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* In this and all subsequent experiments involving iodine, the apparatus was wrapped in aluminium foil to exclude light.

c-2-Azido-t-4-t-Butyl-t-1-iodo-r-1-trimethylsilylcyclohexane.- 4-t-Butyl-1-trimethylsilylcyclohexene (1.05 g, 5 mmol) was treated with iodine (3.05 g, 12 mmol) and lithium azide (0.73 g, 15 mmol) in dry sulpholane (20 ml) and dry chloroform (15 ml) as in the standard method. The crude product was isolated as a reddish-brown liquid (1.5 g, 86%) which solidified after 48 h at 0°C. The solid was recrystallized from light petroleum (b.p. 30-40°C) at -72°C yielding c-2-azido-t-4-t-butyl-t-1-iodo-r-1-trimethylsilylcyclohexane as white crystals, m.p. 29-31°C (Found: C, 41.45; H, 6.9; N, 11.05; I, 32.7. $C_{13}H_{26}N_3SiI$ requires C, 41.5; H, 6.6; N, 10.6; I, 33.45%). δ_H 0.25 (9H,s,$SiMe_3$), 0.9 (9H,s,Bu^t), 1.1-2.4 (7H,m), 4.2 (1H,brs,2-H).

2-Trimethylsilyl-3-methoxycyclohexene.- t-1-Iodo-c-2-methoxy-r-1-trimethylsilylcyclohexane (1.3 g, 4.2 mmol) in dry benzene (20 ml) was added to 1,5-diazabicyclo [5.4.0]undec-5-ene (DBU) (0.64 g, 4.2 mmol) in dry benzene (30 ml). The mixture was stirred and heated under reflux for 6 h. A buff-coloured precipitate slowly formed. The precipitate was filtered off and washed with benzene (10 ml). The washings and filtrate were combined and washed with water (50 ml), brine and dried ($MgSO_4$). Evaporation followed by distillation gave 2-trimethylsilyl-3-methoxycyclohexene (0.42 g, 54%) as a colourless liquid, b.p. 82-84°C at 30 mmHg (Found: C, 64.6; H, 10.7. $C_{10}H_{20}OSi$ requires C, 65.15; H, 10.95%). δ_H 0.0 (9H,s,$SiMe_3$), 1.5-1.8 (4H,m), 1.9-2.0 (2H,m,6-H), 3.25 (3H,s,OMe), 7.7 (1H,brs,3-H), 6.0 (1H,brs,1-H).

3-Azido-2-trimethylsilylcyclohexene.- c-2-Azido-t-1-iodo-r-1-trimethylsilylcyclohexane (2 g, 6.2 mmol), DBU (1.4 g, 9.2 mmol) and dry benzene (40 ml) were heated cautiously under reflux for 6 h. After washing as before with water and brine, the product was isolated as a yellow oil (1.04 g) which was purified by passage as a solution in light petroleum (b.p. 30-40°C) down a short column of silica gel. Evaporation at 18°C gave 3-azido-2-trimethylsilylcyclohexene as a colourless oil (0.72 g, 60%). (Found: C, 54.9; H, 8.75. $C_9H_{17}N_3Si$ requires C, 55.35; H, 8.75%). δ_H 0.1 (9H,s,$SiMe_3$), 1.4-2.4 (6H,m), 3.8 (1H,brs,3-H), 6.3 (1H,brs,1-H).

t-5-t-Butyl-r-3-methoxy-2-trimethylsilylcyclohexene.- t-4-t-Butyl-t-1-iodo-c-2-methoxy-r-1-trimethylsilylcyclohexane (0.56 g, 1.52 mmol) was heated under reflux for 6 h with DBU (0.23 g, 1.52 mmol) and dry benzene (20 ml). The crude product was isolated as a pale yellow oil (0.35 g). Distillation gave t-5-t-butyl-r-3-methoxy-2-trimethylsilylcyclohexene (0.15 g, 41%) as a colourless liquid, b.p. 80°C at 25 mmHg, δ 0.1 (9H,s,$SiMe_3$), 0.9 (9H,s,Bu^t), 1.3-2.4 (5H,m), 3.3 (3H,s,OMe), 3.8 (1H,brs,3-H), 6.2 (1H,brs,1-H). Satisfactory analytical data were not obtained.

Reaction of t-1-Iodo-c-2-methoxy-r-1-trimethylsilylcyclohexane with Lithium Aluminium Hydride in THF.- t-1-Iodo-c-2-methoxy-r-1-trimethylsilylcyclohexane (0.34 g, 1.09 mmol) was heated under reflux with lithium aluminium hydride (0.0625 g, 1.6 mmol) in dry THF (30 ml) for 3 h. G.l.c. (10% PEGA, 65°C) showed two major product peaks in the ratio 1:1 which were identified as cis- and trans-2-methoxy-1-trimethylsilylcyclohexane by coinjection with an authentic sample of the mixture.

7-Aza-1-trimethylsilylbicyclo[4.1.0]heptane.- c-2-Azido-t-1-iodo-r-1-trimethylsilylcyclohexane (0.75 g, 2.3 mmol) in dry ether (1 ml) was added to a stirred slurry of lithium aluminium hydride (0.18 g, 4.6 mmol) in dry ether (10 ml). The mixture was stirred at 18°C for 9 h. Aqueous sodium hydroxide (20 % w/v, 5 ml) was added and stirring continued for 45 min. The liquid was decanted from the solid residue and the latter washed well with ether. The ethereal solution was dried ($MgSO_4$). Evaporation at 18°C gave crude 7-aza-1-trimethylsilylbicyclo-[4.1.0]heptane as a colourless oil (0.3 g, 77%), δ_H -0.05 (9H,s,$SiMe_3$), 1.0-2.1 (10H,m). Distillation and purification by p.l.c. were both unsuccessful.

3-Amino-2-trimethylsilylcyclohexene.- A mixture of 3-azido-2-trimethylsilylcyclohexene (0.72 g, 3.7 mmol), lithium aluminium hydride (0.27 g, 7 mmol) and dry ether (15 ml) was stirred at 18°C for 12 h. Aqueous sodium hydroxide (20% w/v, 5 ml) was added and stirring was continued for 45 min. The ethereal solution was decanted off and shaken with dilute hydrochloric acid (2M, 10 ml). The aqueous layer was separated and aqueous sodium hydroxide (20% w/v) added until the solution was pH 14. The solution was extracted with ether (3 x 15 ml). The ethereal solution was washed with brine and dried ($MgSO_4$). Evaporation of the solvent followed by distillation gave 3-amino-2-trimethylsilylcyclohexene (0.3 g, 41.5%) as a colourless liquid, b.p. 84-86°C at 50 mmHg. (Found: C, 63.7; H, 11.25; N, 8.35. $C_9H_{19}NSi$ requires C, 63.8; H, 11.3; N, 8.25%). δ_H 0.1 (9H,s,$SiMe_3$), 1.1-2.1 (8H,m), 3.4 (1H,brs,3-H), 6.0 (1H,brs,1-H), ν_{max} 3300 (br, N-H), 1610 (C=C), 1250, 850 cm^{-1} (C-Si).

7-Aza-8-methoxy-9-thia-1-trimethylsilylbicyclo[4.3.0]non-7-ene. t-1-Iodo-c-2-isothiocyanato-r-1-trimethylsilylcyclohexane (0.5 g, 1.48 mmol) in ether (10 ml) was added to a solution of potassium hydroxide (0.16 g, 2.96 mmol) in methanol (6 ml). The mixture was stirred at 18°C for 12 h. Water (20 ml) was added and the mixture was extracted with ether (2 x 20 ml). The ethereal extracts were washed with brine and dried ($MgSO_4$). Evaporation of the ether gave a yellow liquid (0.16 g, 45%), which subsequently solidified. Recrystallization from light petroleum (b.p. 30-40°C) at -70°C gave the thiazoline as yellow crystals, m.p. 80-82°C (Found: C, 54.8; H, 8.3; N, 5.8; S, 13.3. $C_{11}H_{21}ONSSi$ requires C, 54.3; H, 8.7; N, 5.8; S, 13.2%). δ_H 0.0 (9H,s,$SiMe_3$), 1.1-2.4 (8H,m), 2.7 (1H,d,*J* 5Hz, 6-H), 3.95 (3H,s,OMe).

N-(2-Trimethylsilylcyclohex-1-en-3-yl)O-methylthiocarbamate.- 3-Isothiocyanato-2-trimethylsilylcyclohexene (0.25 g, 1.18 mmol) in ether (15 ml) was added to potassium hydroxide (0.2 g, 3.6 mmol) in methanol (4 ml). The mixture was stirred at 18°C for 6 h. Water (20 ml) was added and the mixture extracted with ether (2 x 20 ml). The ethereal extracts were washed with brine and dried ($MgSO_4$). The product was isolated as a yellow oil (0.19 g, 66%) which subsequently solidified. It was recrystallized from light petroleum (b.p. 30-40°C) at -72°C giving N-(2-trimethylsilylcyclohex-1-en-3-yl)O-methylthiocarbamate as a yellow crystalline solid, m.p. 80°C. (Found: C, 54.9; H, 8.9; N, 5.8. $C_{11}H_{21}ONSSi$ requires C, 54.3; H, 8.7; N, 5.75%). δ_H 0.02 (9H,s,$SiMe_3$), 1.5 - 2.3 (6H,m), 3.92 (3H,s,OMe), 4.8 (1H,br,NH), 6.2 (1H,brs,1-H).

t-1-Iodo-c,t-2,6-dimethoxy-r-1-trimethylsilylcyclohexene.- 2-Trimethylsilyl-3-methoxycyclohexene (2.2 g, 12 mmol) was treated with iodine (7.32 g, 28.8 mmol) in dry methanol (25 ml) and dry sulpholane (25 ml). A yellow oil was obtained (3.72 g, 90.5%). Purification of a sample by p.l.c. using light petroleum-ether (4:1) gave a yellow crystalline solid which was recrystallized from light petroleum (b.p. 30-40°C) at -72°C giving t-1-iodo-c,t-2,6-dimethoxy-r-1-trimethylsilylcyclohexane m.p. 38-39°C (Found: C, 38.6; H, 6.9. $C_{11}H_{23}O_2SiI$ requires C, 38.6; H, 6.75%). δ_H 0.2 (9H,s,$SiMe_3$), 1.2-2.7 (6H,m), 3.22 (3H,s,OMe), 3.35 (3H,s,OMe), 3.1-3.6 (1H,m,6-H), 3.75 (1H,brs,2-H).

1,3-Dimethoxy-2-trimethylsilylcyclohex-1-ene.- t-1-Iodo-c,t-2,6-dimethoxy-r-1-trimethylsilylcyclohexane (3 g, 8.8 mmol) was heated under reflux with DBU (1.5 g, 9.9 mmol) in dry benzene (50 ml) for 20 h. The precipitated salts were filtered off and the filtrate was washed with water (10 ml) and brine and was dried ($MgSO_4$). Evaporation gave a brown oil (2.4 g) which was distilled to give 1,3-dimethoxy-2-trimethylsilylcyclohex-1-ene (0.85 g, 43%), b.p. 88-90°C at 30 mmHg. (Found: C, 61.0; H, 10.1. $C_{11}H_{22}O_2Si$ requires C, 61.65; H, 10.35%) δ_H 0.05 (9H,s,$SiMe_3$), 1.5-2.4 (6H,m), 3.25 (3H,s,OMe), 3.45 (3H,s,OMe), 3.75 (1H,brs,3-H).

Reaction of 1,3-Dimethoxy-2-trimethylsilylcyclohex-1-ene with Dilute Sulphuric Acid.- Dilute sulphuric acid (20 ml, 0.0625% v/v) and 1,3-dimethoxy-2-trimethylsilylcyclohex-1-ene (0.05 g, 0.23 mmol) in ether (20 ml) were stirred at 18°C for 1.5 h. Sodium carbonate (1 g) and ether (50 ml) were added. The ethereal layer was separated, washed with brine and dried ($MgSO_4$). Evaporation gave an oil (0.046 g) which subsequently crystallized, δ_H 0.05 (9H,s,$SiMe_3$), 1.6-2.5 (6H,m), 7.05 (1H,brs,3-H), ν_{max} (film) 1670 (C=O), 1590 cm^{-1} (C=C) uv (C_2H_5OH) 232 nm, and was considered to be mainly 2-trimethylsilylcyclohex-2-enone (estimated yield by uv 41%). Coinjection with an authentic sample on g.l.c. (3% silicone oil, 140°C) showed a single peak.

Reaction of 2-Trimethylsilylhept-1-ene with Iodine and Methanol. - 2-Trimethylsilylhept-1-ene [0.85 g, 5 mmol; obtained[16] by silylation (Na/Me_3SiCl) of 2-chlorohept-1-ene itself prepared[16] by treatment of 2,3-dichloropropene with Bu.Cu.BF_3[17]] was treated with iodine (3.05 g, 12 mmol) in dry methanol (40 ml) and dry sulpholane (20 ml) as in the standard procedure. The crude product was a brown oil (1.0 g). N.m.r. indicated it to be a mixture of a single adduct (estimated yield 58%) and heptan-2-one (estimated yield 12%) in an approximate ratio of 5:1. A small sample was subjected to p.l.c. using light petroleum-ether (7:3). This gave the adduct, 2-iodo-1-methoxy-2-trimethylsilylheptane as a pale brown oil. (Found: C, 40.6; H, 7.75. $C_{11}H_{25}OSiI$ requires C, 40.25; H, 7.65%). δ_H 0.2 (9H,s,$SiMe_3$), 0.8-1.8 (11H,m), 3.3 (3H,s,OMe), 3.65 (2H,s,1-H).

Reaction of 2-Trimethylsilylhept-1-ene with Iodine and Lithium Azide. 2-Trimethylsilylhept-1-ene (0.85 g, 5 mmol) was treated with iodine (3.05 g, 12 mmol) and lithium azide (0.735 g, 15 mmol) in dry chloroform (25 ml) and dry sulpholane (25 ml). A yellow oil (1.19 g) was obtained, which was redissolved in light petroleum (b.p. 30-40°C) (30 ml) and washed with water (30 ml), to remove residual sulpholane, and brine and dried ($MgSO_4$). Evaporation gave a brown oil (0.55 g), which was subjected to p.l.c. using light petroleum. Two fractions were obtained. The more mobile component on p.l.c. was a brown oil considered to be 1-azido-2-iodo-2-trimethylsilylheptane (0.1 g). (Found: C, 36.3; H, 6.9; N, 11.75; I, 37.95. $C_{10}H_{22}N_3SiI$ requires C, 35.4; H, 6.55; N, 12.4; I, 37.4%), δ_H 0.25 (9H,s,$SiMe_3$), 0.8-1.9 (11H,m), 3.8 (2H,s,1-H). The less mobile component on p.l.c. was a brown oil (0.03 g) tentatively considered to be 2,2-diazido-1-iodoheptane (Found: C, 28.15; H, 4.4; N, 25.05; I, 37.7. $C_7H_{13}N_6I$ requires C, 27.3; H, 4.25; N, 27.3; I, 41.2%) δ_H ($CDCl_3$) 0.8-1.7 (11H,m), 7.35 (2H,s,1-H).

Reaction of 2-Trimethylsilylhept-1-ene with Iodine and Lithium Thiocyanate.- 2-Trimethylsilylhept-1-ene (0.85 g, 5 mmol) was treated with iodine (3.05 g, 12 mmol) in dry chloroform (25 ml) and dry sulpholane (25 ml) using the standard method. A brown oil (1.04 g) was obtained, δ_H ($CDCl_3$) 0.3 (s,$SiMe_3$), 0.8-2.6 (m), 3.89 (q), 5.5 (brs), ν_{max} (film) 2160 (-S-C≡N), 1620 cm^{-1} (C=C), indicating that it consisted of 2-thiocyanatohept-1-ene and 2-iodo-1-thiocyanato-2-trimethylsilylheptane in a ratio of approximately 1:2 (estimated yields 24% and 48% respectively). After 21 days at 18°C, the n.m.r. spectrum of the mixture indicated that the adduct had decomposed to form 2-iodohept-1-ene. A solution of the mixture in ether (1 ml) was passed down a short alumina column, which was eluted first with light petroleum (b.p. 30-40°C) (30 ml) and then with ether/light petroleum (b.p. 30-40°C) (1:99). The first eluant gave an oil (0.1 g), δ_H 0.8-2.6 (11H,m), 5.5 (2H,brs,1-H), ν_{max} (film) 2160 (-S-C≡N), 1620 cm^{-1} (C=C), which was considered to be 2-thiocyanatohept-1-ene. The second eluant gave a yellow oil (0.1 g), δ_H ($CDCl_3$) 0.6-1.6 (9H,m), 2.2-2.5 (2H,m), 5.6 (1H,brs,1-H), 5.9 (1H,brs,1-H), ν_{max} (film) 1620 cm^{-1} (C=C), considered to be 2-iodohept-1-ene.

Reaction of α-Trimethylsilylstyrene with Iodine and Methanol.- α-Trimethylsilylstyrene (0.88 g, 5 mmol) was treated with iodine (3.05 g, 12 mmol) in dry methanol (50 ml) and dry sulpholane (20 ml) by the standard method. A brown oil was obtained (0.74 g), considered to be mainly acetophenone on the basis of: δ_H 2.57 (3H,s,Me), 7.3-7.6 (3H,m.ArH), 7.8-8.1 (2H,m.ArH), ν_{max} (film) 1685 cm^{-1} (C=O).

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