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SYMMETRY ALLOWED $\pi^4s + \pi^2s$ ADDITIONS SILACYCLOPENTADIENES

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Abstract – $\pi^4s + \pi^2s$ cycloaddition of hexaphenylsilacyclopentadiene with ethyl acrylate gives rise to a bicyclosilaheptene derivative. High resolution NMR studies have shown that the ester group in this adduct is in the *endo* position and that the ester methylene protons are magnetically inequivalent. Similar cycloadditions of hexaphenylsilacyclopentadiene, 1,1-dimethyl-2,3,4,5-tetraphenylsilacyclopentadiene, 1-methyl-1,2,3,4,5-pentaphenylsilacyclopentadiene, and 1-methyl-1-vinyl-2,3,4,5-tetraphenylsilacyclopentadiene with dienophiles like acrylonitrile, maleic anhydride and dibenzoylacetylene have been carried out. The stereochemistry of these adducts has been deduced on the basis of NMR studies. Mass spectral fragmentation studies of some of the silabicycloheptenes have been carried out.

Silacyclopentadienes are reported to be formed by the reaction of 1,4-dilithiobutadiene derivatives with suitable dihalosilanes.[1-13] It has been shown that some of these silacyclopentadienes undergo 4+2 cycloaddition reactions giving rise to simple 1:1 adducts. Thus, 1,1-dialkyl or diaryl-2,3,4,5-tetraphenylsilacyclopentadienes add to different dienophiles such as dimethyl acetylenedicarboxylate, benzyne and maleic anhydride to give the corresponding silabicycloheptadienes and silabicycloheptenes, respectively.[3,5,14,15] Laporterie *et al.*[16] have recently shown that substituted acetylenes like 1-trichlorosilylethyne and 1-trichlorogermylethyne react with 1,1-dimethyl-2,5-diphenylsilacyclopentadiene to give the corresponding 4+2 adducts. An interesting case where a silacyclopentadiene acts as a dienophile is observed in the reaction of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene with 2,3-dimethyl-1,3-butadiene to give 1,8-diphenyl-3,4,9,9-tetramethyl-9-silabicyclo[4.3.0]-nona-3,7-diene.[17]

Although the 4+2 cycloadditions of few silacyclopentadienes with different dienophiles have been reported, doubts have been raised concerning the structure of some of these addition compounds. Thus, for instance, Maruca has suggested that the addition product from the reaction of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene with tolan is not a "true adduct" but a 1:1 solid complex.[17] Recent X-ray studies by Clardy and Barton[18] support this view. They have shown that in the 1:1 crystal complex, each tolan molecule is surrounded by four silacyclopentadiene molecules and that the average distance of the potential Diels-Alder bonds is 5·11Å. The object of the present investigation was to study the symmetry allowed $\pi^4s + \pi^2s$ additions of few representative silacyclopentadienes with a view to examining the nature of the adducts formed in these reactions and also the stereochemistry of some of these adducts. The silacyclopentadienes that we have chosen for our studies include hexaphenylsilacyclopentadiene (**1a**), 1-methyl-1,2,3,4,5-pentaphenylsilacyclopentadiene (**1b**), 1,1-dimethyl-2,3,4,5-tetraphenylsilacyclopentadiene (**1c**) and 1-methyl-1-vinyl-2,3,4,5-tetraphenylsilacyclopentadiene (**1d**). Of these, hexaphenylsilacyclopentadiene[3] and 1,1-dimethyl-2,3,4,5-tetraphenylsilacyclopentadiene[5] were reported earlier. Also, the preparation of 1-methyl-1,2,3,4,5-pentaphenylsilacyclopentadiene was attempted earlier through the reaction of 1,2,3,4,5-pentaphenylsilacyclopentadiene with a mixture of bis(trimethylsilyl)sodamide and dimethyl sulphate.[19] In the present studies, we have prepared both **1b** and **1d** through the reaction of 1,4-dilithio-tetraphenylbutadiene with the corresponding dichlorosilanes in 74 and 55% yields, respectively.

The thermal additions of **1a–d** with different dienophiles were carried out by direct heating of the reactants in the absence of any solvent. The reaction of **1a** with excess of ethyl acrylate, for example, gave a 55% yield of a 1:1 adduct, m.p. 226–227° (d). The structure of this adduct was established as ethyl 1,4,5,6,7,7-hexaphenyl-7-silabicyclo[2.2.1]-hept-5-ene-2-carboxylate (**2a**). Similarly, the reaction of **1a** with acrylonitrile and dibenzoylacetylene gave the corresponding 1:1 adducts, **3a** and **5a** in 88 and 35% yields, respectively. Likewise, 1:1 adducts were formed in good yields in the reactions of **1b–d** with dienophiles such as ethyl acrylate, acrylonitrile, dibenzoylacetylene and maleic anhydride (Scheme 1). The

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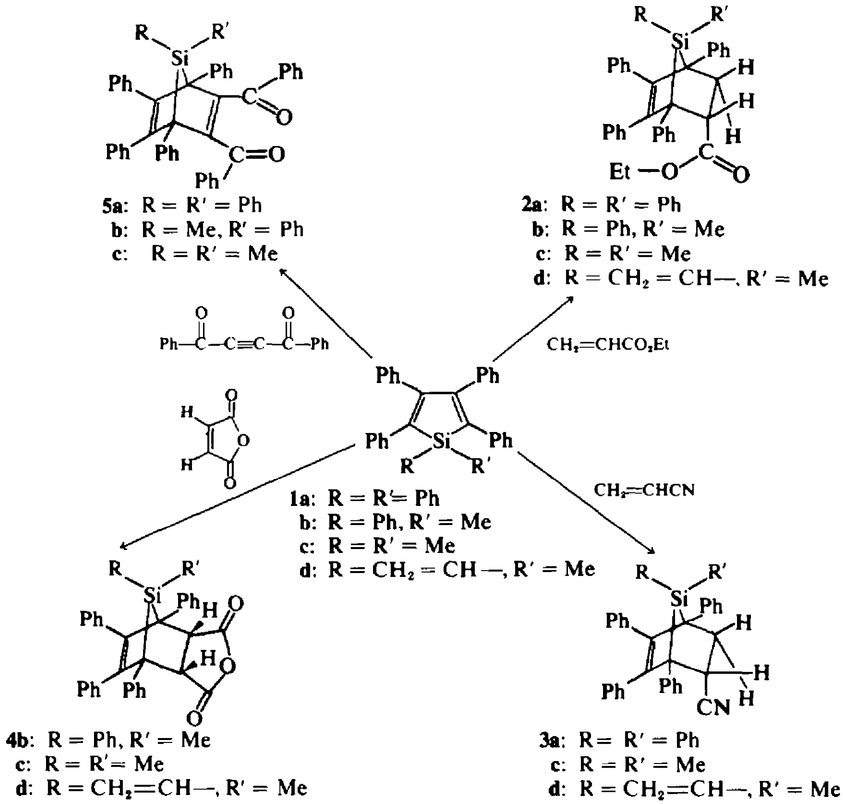


SCHEME 1

structures of these adducts were proved as 7-silabicyclo[2.2.1]-heptenes and heptadienes, on the basis of analytical results and spectral data.

Stereochemistry of 7-silabicyclo[2.2.1]-hept-5-enes

Ethyl 1,4,5,6,7,7-hexaphenyl-7-silabicyclo[2.2.1]-hept-5-ene-2-carboxylate (**2a**) formed from the reaction of **1a** with ethyl acrylate can have either an *endo* or *exo* configuration as far as the carbethoxyl group is concerned. With a view to studying the stereochemistry of this adduct, we have examined its NMR spectrum. A 60 MHz NMR spectrum of **2a** shows a triplet at 1·28δ(3H), a broad doublet around 2·85δ(2H) and a broad multiplet centred around 4·18δ(3H). In addition, the phenyl protons appear as a broad multiplet centred around 7·21δ (30H). A high-resolution NMR spectrum of **2a** (250 MHz) (Fig 1) shows the broad doublet around 2·85δ as a clearly resolved 8-line multiplet. Similarly, the broad multiplet around 4·18δ appears as a 20-line multiplet (Fig 2). Analysis of the NMR spectrum reveals that the 8-line multiplet can be assigned to the methylene protons at the C_3-position (H_A and H_B). The geminal coupling between these two protons (J_{AB}) has been found to be 12·5 Hz. The C_3-protons are further split by the methine proton at the C_2-position (H_C) and the coupling constants J_{AC} and J_{BC} are found to be 6·0 Hz and 9·5 Hz, respectively.

Of the 20 lines in the multiplet around 4·18δ(3H), four lines are assigned to the C_2 methine proton. The remaining 16 lines could be due to the ester methylene protons (H_D and H_E), if we assume that they are magnetically inequivalent. Irradiation of the ester Me protons has shown that the 20-line multiplet simplifies to an 8-line spectrum (Fig 3), consisting of one quartet, due to the C_2 methine proton and a pair of doublets due to the methylene protons (H_D and H_E). The very fact that the ester methylene protons, H_D and H_E appear as a pair of doublets shows that these two protons are magnetically inequivalent. The geminal coupling constant between H_D and H_E (J_{DE}) is found to be 10·5 Hz, whereas, the coupling of these protons with the adjacent Me protons (H_X) is 7·3 Hz and 7·0 Hz, respectively ($J_{DX} = 7 \cdot 3$ Hz, $J_{EX} = 7 \cdot 0$ Hz). One of the possible reasons for the magnetic inequivalence of the ester methylene protons (H_D and H_E) in **2a** could be due to the absence of free rotation of the carbethoxyl group due to the Ph substituent at C_1-position. Such inequivalence of methylene protons due to restricted rotation has been reported earlier in other systems.[20,21] Examination of the molecular models reveals that such a restricted rotation of the

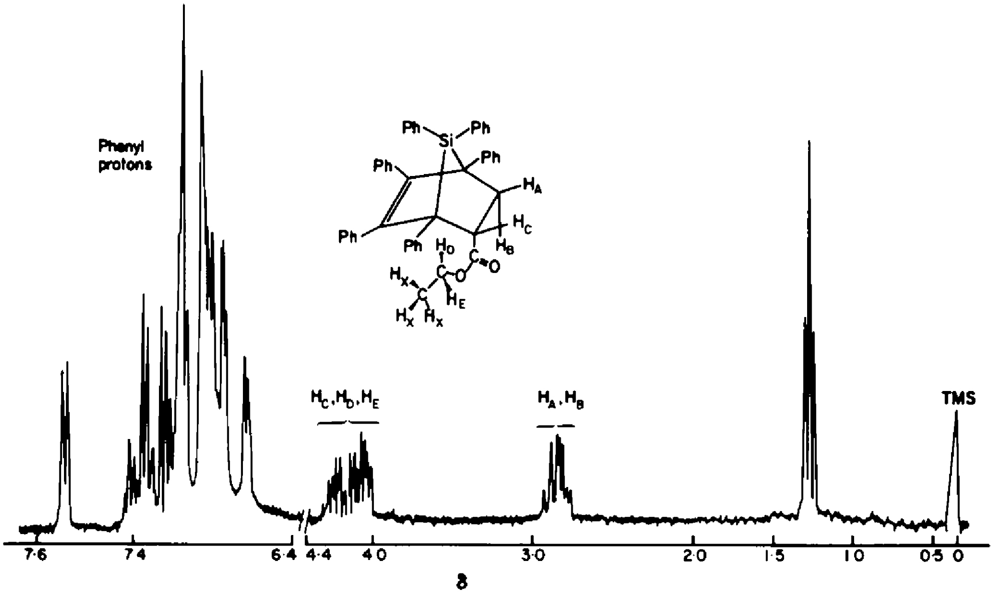


Fig 1.

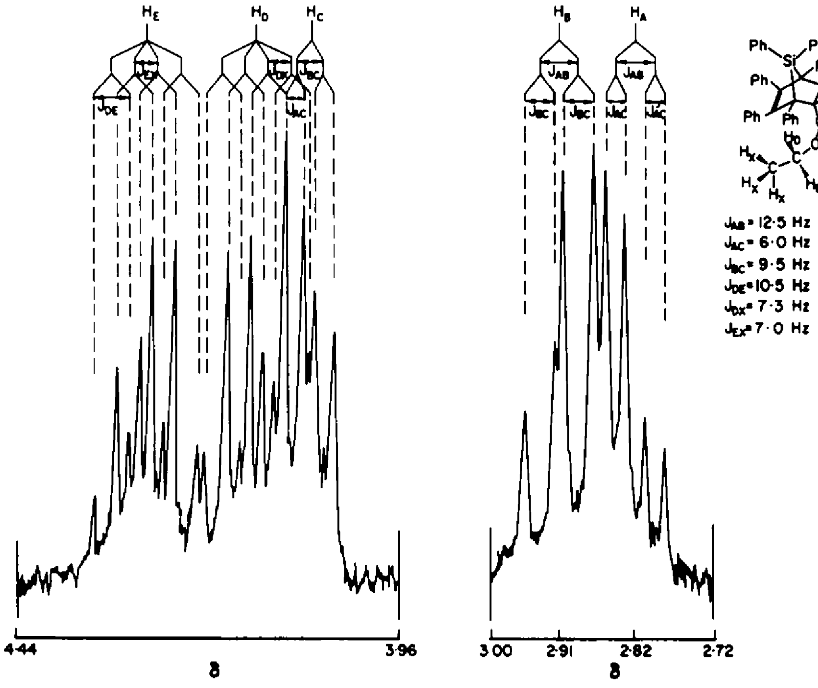


Fig 2.

carbethoxyl group is feasible only if this group is present in the *endo* position. Hence, we can indirectly deduce the configuration of **2a** as the *endo*-isomer. Such a stereochemistry for **2a** would be predicted in terms of orbital symmetry also, provided we assume that secondary orbital interactions between the ester carbonyl group and the silacyclopentadiene system are playing some role.

In the reaction of an unsymmetrically substituted silacyclopentadiene such as 1-methyl-1,2,3,4,5-pentaphenylsilacyclopentadiene (**1b**) with a dienophile such as ethyl acrylate, two possible

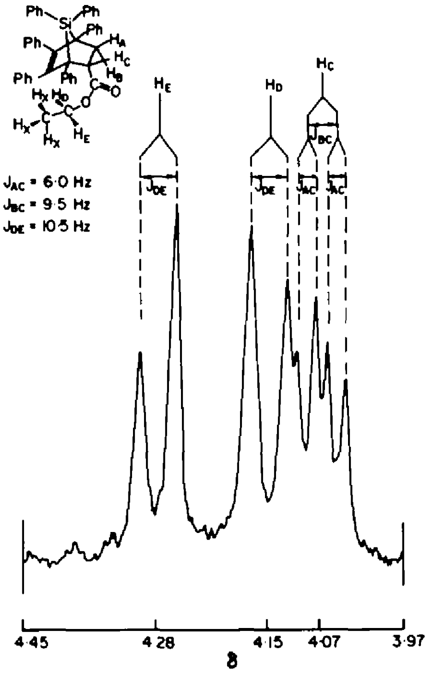
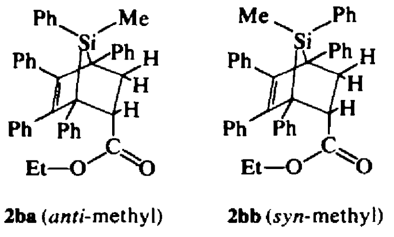


Fig 3.

silabicycloheptenes can result, even if we assume an *endo* configuration for the carbethoxyl group. In one of these adducts (**2ba**), the Me group will be *anti* with respect to the double bond, whereas, in the other (**2bb**), the Me group will be in a *syn* geometry (Scheme 2). In the *syn* isomer (**2bb**) the Si–Me protons are in the shielding region of the olefinic double bond and hence one would expect a slight upfield shift of these protons in its NMR spectrum, as compared to the chemical shift of the Si–Me protons in the *anti* isomer (**2ba**). In order to assess the extent of such shielding effects in silabicycloheptene systems, we have examined the NMR spectra of several such adducts and the chemical shifts of the various protons are listed in Table 1. The NMR spectrum of ethyl 7,7-dimethyl-1,4,5,6-tetraphenyl-7-silabicyclo[2.2.1]-hept-5-ene-2-carboxylate (**2c**), for example, shows two singlets at 0·57δ(3H) and 0·16δ(3H) due to the two Si–Me protons. Of these, the signal at 0·16δ is assigned to the Si–Me protons *syn* to the double bond and hence more shielded than the Si–Me protons which are *anti* to the double bond.



2ba (*anti*-methyl) **2bb** (*syn*-methyl)

Scheme 2

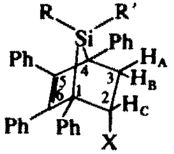
The NMR spectrum of **2b** shows the Si–Me protons as a singlet at 0·44δ. Based on the chemical shift assignment of Si–Me protons in **2c**, we infer that the Si–Me group in **2b** is not shielded and hence the adduct may have the *anti*-configuration (**2ba**) as shown in Scheme 2. However, it might be pointed out that such an assignment has to be tentative only, since the chemical shift of Si–Me groups may be influenced through the Ph substitution on the same silicon atom.

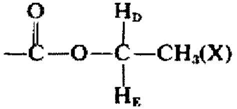
Similarly, the 1 : 1 adduct (**2d**), obtained from the reaction of 1-methyl-1-vinyl-2,3,4,5-tetraphenylsilacyclopentadiene with ethyl acrylate can have either the *syn*-Me or *anti*-Me configuration. The NMR spectrum of **2d** shows a sharp singlet at 0·66δ(3H) due to the Si–Me protons. The relatively downfield shift of these protons would indicate that the adduct **2d** has the *anti*-Me configuration. The vinylic protons in **2d** appear as a multiplet around 6·03δ(3H).

We have examined the 250 MHz NMR spectra of the silabicycloheptene adducts **2b** and **2c** also and found that the ester methylene protons in these adducts are magnetically inequivalent, just as in the case of **2a**. In all these cases, the ester methylene protons and the C_2-methine proton appear as 20-line multiplets in the range of 4·18–4·26δ (Table 1). The C_3-methylene protons (H_A and H_B) in the adduct **2c** appear as an 8-line multiplet around 2·80δ, whereas, in adduct **2b**, they appear as a doublet around 2·85δ. The appearance of this doublet in **2b** would suggest that there is an accidental degeneracy as far as H_A and H_B protons are concerned. The magnetic inequivalence of the ester methylene protons in **2b** and **2c** would suggest that in all these adducts the ester groups are in the *endo* configuration, as in **2a**. In the case of the adduct **2d**, the NMR spectrum (60 MHz) shows a broad multiplet around 2·88δ(2H) due to the C_3-methylene protons and a broad multiplet around 4·26δ(3H) due to the ester methylene protons and the C_2-methine proton which is similar to the NMR spectra (60 MHz) of the adducts **2a–c** in the corresponding region. Hence, by analogy, it can be assumed that the ester methylene protons in the adduct **2d** are also magnetically inequivalent and that the ester group has an *endo* configuration.

The NMR spectrum of the silabicycloheptene **3a** reveals that the C_3-methylene protons (H_A and H_B) appear as two quartets around 2·79δ, whereas, the C_2-methine proton appears as a quartet around 4·12δ (J_{AB} = 13·0 Hz, J_{AC} = 5·5 Hz and J_{BC} = 10·0 Hz). On the basis of analogy to the ethyl acrylate adducts (**2a–d**), we assume that the cyano group in this adduct is in the *endo* configuration. In the silabicycloheptene adduct **3c**, the Si–Me protons

Table 1. NMR chemical shifts and coupling constants of protons in 7-silabicyclo[2.2.1]-hept-5-enes*



Compound	Phenyl protons	Substituents on silicon			Protons at C_2 and C_3 positions			 $-\overset{\overset{O}{\|}}{C}-O-\underset{\underset{H_E}{\|}}{\overset{\overset{H_D}{\|}}{C}}-CH_3(X)$			Coupling constants (Hz)					
		CH_3	CH_3	$CH_2{=}CH-$	H_A	H_B	H_C	H_D	H_E	H_X	J_{AB}	J_{AC}	J_{BC}	J_{DE}	J_{DX}	J_{EX}
2a†	7·21 (m, 30H)	—	—	—	2·82 (q, 1H)	2·91 (q, 1H)	4·07 (q, 1H)	4·14 (m, 1H)	4·28 (m, 1H)	1·28 (t, 3H)	12·50	6·00	9·50	10·50	7·30	7·00
2b†	7·19 (m, 25H)	0·44 (s, 3H)	—	—	2·85 (d, 2H)		4·28 (t, 1H)	4·18 (m, 1H)	4·29 (m, 1H)	1·29 (t, 3H)	—	8·00	8·00	11·50	7·25	7·00
2c†	6·99 (m, 20H)	0·57 (s, 3H)	0·16 (s, 3H)	—	2·76 (q, 1H)	2·83 (q, 1H)	4·14 (q, 1H)	4·15 (m, 1H)	4·25 (m, 1H)	1·27 (t, 3H)	12·50	6·00	9·50	10·80	7·25	7·00
2d	7·10 (m, 20H)	0·66 (s, 3H)	—	6·03 (m, 3H)	2·88 (m, 2H) poorly resolved			4·26 (m, 3H) poorly resolved		1·28 (t, 3H)	—	—	—	—	—	—
3a	7·33 (m, 30H)	—	—	—	2·70 (q, 1H)	3·10 (q, 1H)	3·98 (q, 1H)	—	—	—	12·50	5·50	9·50	—	—	—
3c	7·04 (m, 20H)	0·70 (s, 3H)	0·14 (s, 3H)	—	2·73 (q, 1H)	3·16 (q, 1H)	4·11 (q, 1H)	—	—	—	13·00	5·50	10·00	—	—	—
3d	7·09 (m, 20H)	—	0·26 (s, 3H)	6·78 (m, 3H)	2·78 (q, 1H)	3·18 (q, 1H)	4·12 (q, 1H)	—	—	—	13·00	5·50	9·50	—	—	—
4b	7·39 (m, 25H)	0·57 (s, 3H)	—	—	4·68 (s, 2H)			—	—	—	—	—	—	—	—	—
4c	6·90 (m, 20H)	0·67 (s, 3H)	0·28 (s, 3H)	—	4·47 (s, 2H)			—	—	—	—	—	—	—	—	—
4d	7·68 (m, 20H)	0·58 (s, 3H)	—	6·75 (m, 3H)	4·68 (s, 2H)			—	—	—	—	—	—	—	—	—

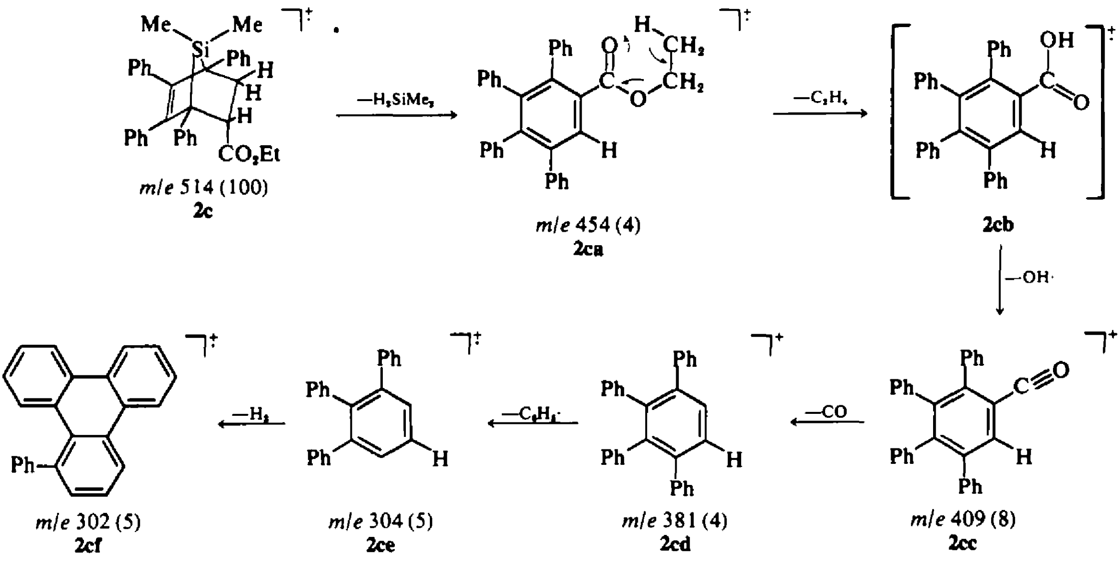
*All the peak positions are in δ units and the spectra were run in $CDCl_3$ using TMS as internal standard.
†250 MHz spectral data.
s—singlet; d—doublet; t—triplet; q—quartet and m—multiplet.

appear as two singlets at 0·70δ and 0·14δ, respectively. Of these, the signal at 0·70δ is assigned to the Me group *anti* to the double bond, whereas, the upfield signal at 0·14δ is assigned to the more shielded *syn*-Me protons. In the case of the unsymmetrically substituted adduct **3d**, we find that the Si–Me group appears at 0·26δ. This relatively upfield shift of the Si–Me protons would suggest a *syn*-geometry for the Me group in this adduct.

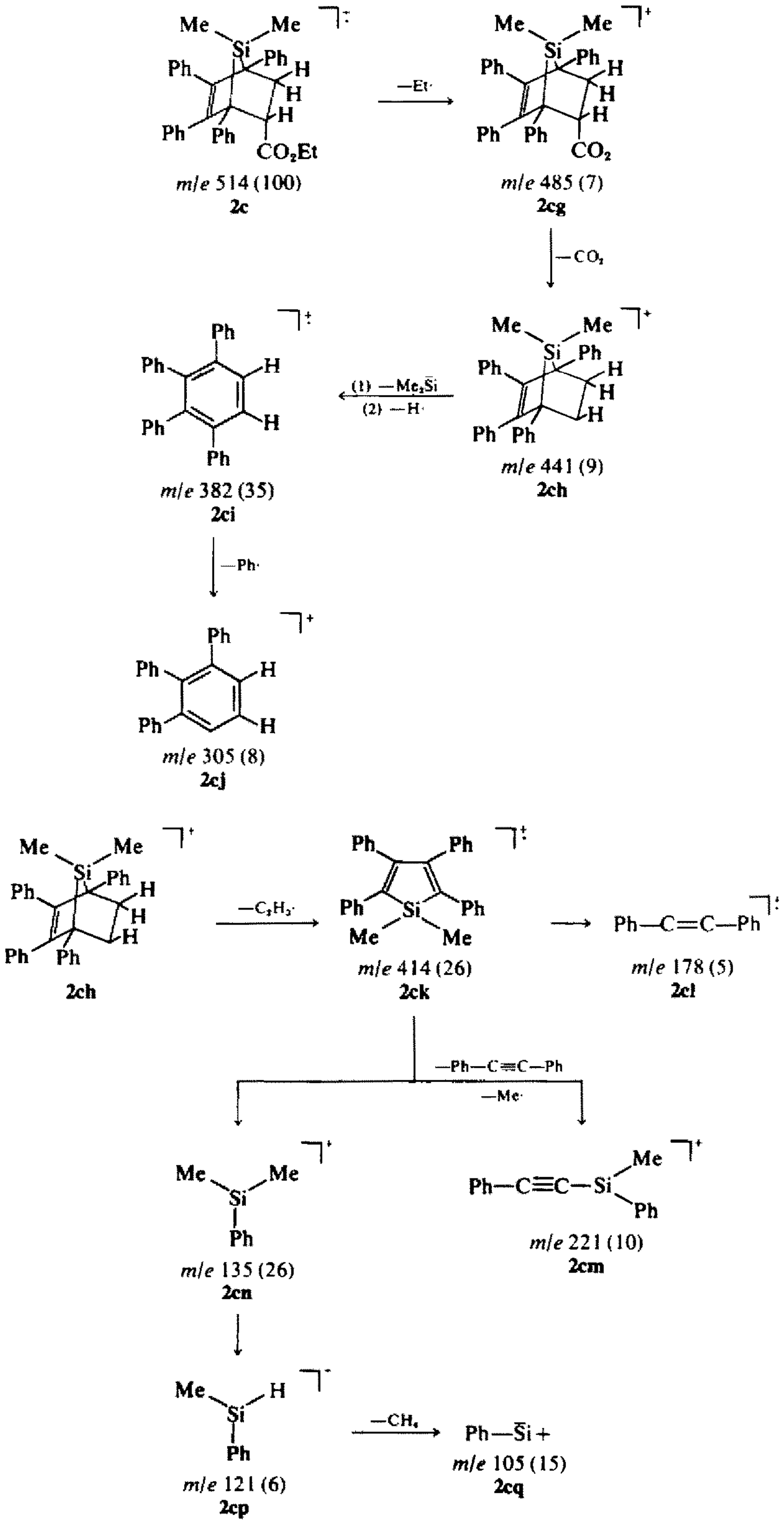
The silabicycloheptene derivatives **4b–d**, formed from the reaction of the corresponding silacyclopentadienes with maleic anhydride, would be expected to have the *endo* configurations, on the basis of analogy to the adducts **2a–d** and **3a,c,d**. The NMR spectrum of **4b**, shows a singlet at 0·57δ due to the Si–Me protons and another singlet at 4·68δ (2H) due to the two methine protons at C_2 and C_3 positions. On the basis of the chemical shift of the Si–Me protons, an *anti*-Me configuration is assigned to the adduct **4b**. The NMR spectrum of **4c**, on the other hand, shows two sets of singlets for the Si–Me protons; one at 0·28δ due to the *syn*-Me group and the other at 0·67δ due to the *anti*-Me group. The chemical shift of the Si–Me protons in the unsymmetrically substituted adduct **4d** is found to be 0·58δ, which is indicative of an *anti*-Me configuration for this adduct.

On the basis of the configurational assignments of the silabicycloheptenes **2b**, **2d**, **3d**, **4b** and **4d**, we find that the approach of the dienophile in the 4 + 2 cycloadditions of the unsymmetrically substituted silacyclopentadienes **1b** and **1d**, takes place from the less hindered side. In the case of **1b**, where the substituents on silicon are Me and Ph, the approach of the dienophile appears to be from the Me side leading to adducts **2b** and **4b**, respectively. In the reaction of 1-methyl-1-vinyl-2,3,4,5-tetraphenylsilacyclopentadiene with dienophiles, however, no such selectivity is observed. Thus, in the formation of adducts **2d** and **4d**, the dienophiles approach from the Me side, whereas, in the case of the adduct **3d**, the dienophile appears to approach from the vinyl side of the starting silacyclopentadiene.

Mass spectral fragmentations of 7-silabicyclo-[2.2.1]-hept-5-enes. Maruca *et al.*[22] have recently studied the mass spectral fragmentation of few silicon heterocycles such as 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene, 1,1-dimethyl-2,5-diphenyl-1-silacyclopentane, 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene and 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disila-2,5-cyclohexadiene and have found that different types of rearrangements are initiated in these systems. During the course of the present investigation, we have examined the mass spectral fragmentations of few representative 7-silabicycloheptenes with a view to studying the mode of cleavage in these systems. The adducts that we have examined include **2a**, **2b**, **2c** and **4c**. The mass spectrum of **2c**, for example, shows the molecular ion peak at *m/e* 514 (100%). Other peaks are observed at *m/e* 485(7), 454(4), 441(9), 414(26), 409(8), 382(35), 381(4), 305(8), 304(5), 302(5), 221(9), 178(5), 135(26), 121(6) and 105(15), which could be assigned to some of the fragments shown in Scheme 3. The species at *m/e* 454 has been formulated as **2ca**, formed by the loss of dimethylsilane from the molecular ion (**2c**). Further loss of an ethylene molecule, followed by the loss of a OH radical would lead to the ion **2cc** at *m/e* 409, through the intermediate **2cb**. Such fragmentations of esters of benzoic acid are well documented in the literature.[23] The ready loss of a



SCHEME 3



Scheme 3 (cont.)

Table 2. $\pi^4s + \pi^2s$ cycloadditions of silacyclopentadienes with different dienophiles

	Reaction					Calcd. (%)			Found %			
Cycloadduct	Temp. (°C)	Time (hr)	Yield (%)	M.p. (°C)	Molecular formula	C	H	N	C	H	N	UV λ_{max}, nm (ϵ)
2a	160–170	24	55	226–227(d)	$C_{45}H_{38}O_2Si$	84·65	5·96	—	84·88	5·59	—	233(31,700), 278(11,100) 295(7,700)
2b	110–115	8	55	212–213(d)	$C_{40}H_{36}O_2Si$	83·33	6·25	—	83·35	6·02	—	234(26,600), 276(9,300) 293(8,100)
2c	105–110	20	82	177–178(d)	$C_{35}H_{34}O_2Si$	81·70	6·62	—	81·46	6·53	—	235(28,100), 279(11,100)
2d	110–115	10	30	173–174	$C_{38}H_{34}O_2Si$	82·14	6·47	—	81·90	6·55	—	234(25,700), 278(8,700) 290(8,000)
3a	130–135	10	88	255–256(d)	$C_{43}H_{33}NSi$	87·31	5·58	2·37	87·36	5·70	2·63	226(39,000), 278(9,700) 287(7,200), 297(6,500)
3c	135–140	10	45	188–189(d)	$C_{33}H_{29}NSi$	84·80	6·21	3·00	84·90	6·16	3·32	218(19,500), 254(9,600)
3d	70–80	10	65	215–216(d)	$C_{34}H_{29}NSi$	85·19	6·05	2·92	85·09	6·05	3·05	232(21,900), 276(9,000)
4b	100–105	5	60	205–206	$C_{39}H_{30}O_3Si$	81·53	5·23	—	81·55	5·42	—	218(33,000), 266(8,800) 291(7,300)
4c	110–115	4	72	237–238(d)	$C_{34}H_{28}O_3Si$	79·69	5·47	—	79·70	5·81	—	227(28,200), 272(9,900)
4d	100–105	4	55	196–197(d)	$C_{35}H_{28}O_3Si$	80·15	5·34	—	79·96	5·20	—	226(32,400), 277(9,000) 287(8,000)
5a	120–130	24	35	263–264(d)	$C_{56}H_{40}O_2Si$	87·06	5·18	—	87·08	4·83	—	233(42,300), 294(13,300) 387(49,400)
5b	100–110	6	45	244–245	$C_{51}H_{38}O_2Si$	86·20	5·35	—	85·56	5·25	—	284(14,000), 386(6,300)
5c	100	25	20	163–164(d)	$C_{46}H_{36}O_2Si$	85·17	5·56	—	85·55	6·05	—	228(31,500), 286(14,200) 296(13,900), 390(10,200)

molecule of CO from **2cc** would lead to the ion **2cd** at *m/e* 381. The presence of a peak at *m/e* 304 can be attributed to the ion **2ce**, formed by the loss of a Ph radical from **2cc**. Further loss of two H atoms from **2ce** would lead to the ion **2cf** at *m/e* 302.

A second mode of fragmentation of the molecular ion (**2c**) involves the loss of an Et radical resulting in the ion **2cg** at *m/e* 485. Further loss of CO_2 from this ion would give **2ch** at *m/e* 441. The peak at *m/e* 382 can be attributed to the tetraphenylbenzene cation radical (**2ci**). Loss of a Ph group from the ion **2ci** would lead to the formation of **2cj** at *m/e* 305.

An alternative mode of fragmentation of the ion at *m/e* 441 is through the loss of a C_2H_3 residue leading to the formation of the silacyclopentadiene ion **2ck** at *m/e* 414. The peaks at *m/e* 221, 178, 135, 121 and 105 are assigned to fragments **2cm**, **2cl**, **2cn**, **2cp** and **2cq**, respectively, as shown in Scheme 3, which correspond to the reported fragmentation pattern of 1,1-dimethyl-2,3,4,5-tetraphenylsilacyclopentadiene (**1c**).[22]

The mass spectral fragmentations of other 7-silabicycloheptenes, **2a**, **2b** and **4c** are analogous to those of **2c**.

EXPERIMENTAL

All m.ps are uncorrected. The IR spectra were recorded on a Perkin-Elmer, Model 521 Infrared Spectrometer and electronic spectra, on a Beckman, DB Spectrophotometer. NMR traces were recorded on a Varian A-60 spectrometer and in the cases of **2a–c**, on a 250 MHz spectrometer also. The mass spectra were recorded on a Hitachi RMU-6E single focussing mass spectrometer.

Starting materials. Diphenyldichlorosilane, b.p. 295–297°, methylphenyldichlorosilane, b.p. 204–205°, dimethyldichlorosilane, b.p. 70° and methylvinyldichlorosilane, b.p. 92–93° were freshly distilled before use. Tolan, m.p. 60° was prepared by a standard procedure involving the oxidation of benzildihydrazone.[24] The dienophiles, ethyl acrylate, b.p. 98–99°, acrylonitrile, b.p. 76–77° and maleic anhydride, m.p. 53–54° were purified before use. Dibenzoylacetylene, m.p. 110–111° was prepared in an 85% yield by a reported procedure.[25]

Silacyclopentadienes (**1a–d**). In a typical experiment, a mixture of tolan (5·34 g, 30 mmol) and Li (0·21 g, 0·03 g atom) was shaken in diethyl ether (12 ml) for 3 hr, under N_2 in a Schlenk tube. Few clean, broken glass pieces were added in order to ensure a fresh metal surface, during the course of the reaction. This freshly prepared 1,4-dilithiotetraphenylbutadiene adduct was diluted with 80 ml THF and it was added to a soln of diphenyldichlorosilane (3·8 g, 15 mmol) in 10 ml THF, with constant stirring over a period of 15 min under N_2. Removal of the solvent under vacuum gave a product which was extracted with benzene. Removal of the solvent from the benzene-soluble portion gave a product which was recrystallized from cyclohexane to give 5·1 g (64%) of **1a**, m.p. 190–191° (lit.[6] m.p. 190–191°).

Similarly, the reaction of 1,4-dilithio-tetraphenylbutadiene, formed from 7·2 g (40 mmol) of tolan and 0·28 g (0·04 g atom) of Li in THF, with 3·82 g (20 mmol) of methylphenyldichlorosilane gave 7 g (74%) of **1b**, m.p. 173–174°, after recrystallization from light petroleum (b.p. 60–80°) (lit.[19] m.p. 172–173°) (Found: C, 88·18; H, 5·76. $C_{35}H_{28}Si$ requires: C, 88·22; H, 5·88%).

Treatment of 1,4-dilithio-tetraphenylbutadiene with dimethyldichlorosilane gave a 61% yield of **1c**, m.p. 180–181° (lit.[5] m.p. 180–181°).

The reaction of 1,4-dilithio-tetraphenylbutadiene formed from 5·34 g (30 mmol) of tolan and 0·21 g (0·03 g atom) of Li in THF, with 2·15 g (15 mmol) of methylvinyldichlorosilane gave 3·4 g (55%) of **1d**, m.p. 177–178°, after recrystallization from MeOH. (Found: C, 87·26; H, 6·23; $C_{31}H_{26}Si$ requires: C, 87·32; H, 6·05%); IR spectrum (KBr)ν_{max}: 2985, 1600, 1486, 1445, 1299, 1256, 1096, 1081, 1031, 1008, 962, 943, 922, 800, 768, 752, 735, 714 and 700 cm^{-1}; UV spectrum (cyclohexane): 250 nm (ϵ, 26,700) and 360 (8,800); NMR spectrum ($CDCl_3$): 0·55δ (s, 3H, Si–Me), 6·16δ (m, 3H, vinyl) and 6·99δ (m, 20H, phenyl).

Reaction of silacyclopentadienes with dienophiles. In a typical reaction, 0·5 mmol of the silacyclopentadiene and 1 mmol of the dienophile were heated together in a sealed tube over 100° for several hr. The product mixture was washed with light petroleum (b.p. 60–80°) to remove any unchanged dienophile and recrystallized from suitable solvents to constant m.p. Table 2 summarises the experimental details.

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