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PERACID OXIDATION AND PHOTOOXYGENATION REACTIONS OF SILACYCLOPENTADIENES

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Abstract—1-Methyl-1,2,3,4,5-pentaphenyl-1-silacyclopentadiene on treatment with perbenzoic acid afforded a mixture of products consisting of tetraphenylfuran, *cis*-dibenzoylstilbene, *cis*-dibenzoylstilbene epoxide, 2,5-dihydro-2,3,4,5-tetraphenylfuran, 1,2,3-triphenyl-1,3-propanedione, 1-methylphenylhydroxysilyl-1,2,3,4-tetraphenyl-1,3-butadiene and *cis, cis*-1,2,3,4-tetraphenyl-1,3-butadiene. Similarly, hexaphenylsilacyclopentadiene reacted with perbenzoic acid to give a mixture comprising tetraphenylfuran and *cis*-dibenzoylstilbene. Photooxygenation of 1-methyl-1-vinyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene has been found to give a mixture of products including *cis*-dibenzoylstilbene, *trans*-dibenzoylstilbene and isodidesyl. Possible mechanistic pathways for these reactions have been suggested.

Silacyclopentenes are known to undergo epoxidation, on treatment with peracids. Thus, 1,1 - dimethyl - 1 - silacyclopent - 3 - ene,[1,2] 1,1,3 - trimethyl - 1 - silacyclopent - 3 - ene[3] and 1,1 - dimethyl - 2,5 - diphenyl - 1 - silacyclopent - 2 - ene[4] on treatment with peracids give the corresponding epoxides which are further transformed to various products. However, 1,2-disilacyclopentenes[5] and 1,2-disilacyclohexadienes[6] are reported to undergo oxygen insertion reactions leading to cyclic siloxenes, on treatment with peracids.

During the course of our investigations on silacyclopentadienes, we have examined the reaction of perbenzoic acid with some representative silacyclopentadienes with a view to studying the nature of the products formed in these cases. Thus, treatment of 1 - methyl - 1,2,3,4,5 - pentaphenyl - 1 - silacyclopentadiene (**1**) with perbenzoic acid in chloroform, for example, gave a mixture of products consisting of tetraphenylfuran (**7**, 16%), 2,5 - dihydro - 2,3,4,5 - tetraphenylfuran (**10**, 5%), 1 - methylphenyl - hydroxysilyl - 1,2,3,4 - tetraphenyl - 1,3 - butadiene (**11**, 14%), *cis, cis* - 1,2,3,4 - tetraphenyl - 1,3 - butadiene (**12**, 4%), *cis*-dibenzoylstilbene (**13**, 15%), *cis*-dibenzoylstilbene epoxide (**16**, 7%) and 1,2,3 - triphenyl - 1,3 - propanedione (**20**, 5%) (Scheme 1). The identities of these compounds have been established on the basis of spectral evidences and also by comparison with authentic samples.

The structure of **10** has been assigned as 2,5 - dihydro - 2,3,4,5 - tetraphenylfuran on the basis of analytical data and spectral evidences. The NMR spectrum of **10**, for example, shows a singlet at 3.98δ (2H) and a multiplet centered around 7.45δ (20H), suggesting a symmetrical structure for **10**. Further confirmation of the structure of **10** is derived through its mass spectrum which shows the molecular ion peak at *m/e* 374 (100%).

Other peaks appear at *m/e* 297 (15), 296 (9), 283 (17), 269 (33), 268 (19), 267 (11), 192 (15), 191 (71), 178 (24) and 105 (30) which could be assigned to some of the fragments shown in Scheme 2.

Compound **20**, has been identified as 1,2,3 - triphenyl - 1,3 - propanedione on the basis of spectral data. The m.p., IR and electronic spectral characteristics of **20**, are in agreement with those of an authentic sample prepared by a reported procedure.[7] Further confirmation of the structure of **20**, has been derived through its mass spectrum which shows the molecular ion peak at *m/e* 300 (80%). Other peaks are observed at *m/e* 299 (30), 283 (5), 281 (5), 223 (25), 195 (16), 194 (14), 178 (60), 167 (51), 166 (27), 165 (100), 152 (51), 149 (46) and 105 (90) which could be assigned to some of the fragments shown in Scheme 3.

The structure of **11** has been assigned as 1 - methylphenylhydroxysilyl - 1,2,3,4 - tetraphenyl - 1,3 - butadiene on the basis of analytical data and spectral evidences. The NMR spectrum of **11**, for example, shows singlets at 0.62δ (3H, $SiCH_3$) and 2.40δ (1H, SiOH exchanging with D_2O) and multiplet centered around 7.25δ (26H, phenyl). The mass spectrum of **11** shows the molecular ion peak at *m/e* 494 (15%).

The formation of compounds like **7**, **10**, **11**, **12**, **13**, **16** and **20** in the reaction of 1 - methyl - 1,2,3,4,5 - pentaphenyl - 1 - silacyclopentadiene (**1**) with perbenzoic acid could be rationalized in terms of the mechanistic pathways shown in Scheme 1. In this scheme, we presume that the starting silacyclopentadiene, **1** is initially converted to its diepoxide, **3** which is then transformed to 1,2 - dibenzoyl - 1,2 - diphenylethane (**6**). Acid-catalyzed cyclization of **6** would then lead to tetraphenylfuran (**7**). Peroxidation of **7** could give rise to products like *cis*-dibenzoylstilbene (**13**), the ester, **19** and *cis*-dibenzoylstilbene epoxide (**16**) as shown in Scheme 1. The formation of 1,2,3 - triphenyl - 1,3 - propanedione (**20**) could be through the hydrolysis of the enol benzoate, **19**. It might be mentioned in this connection that peracid oxidation of tetraphenylfuran (**7**) has been studied by Lutz *et al.*[8] and Lahiri and George[9] to give a mixture of products consisting of **13**, **16** and **19** under different conditions. It has not been possible to isolate any of the diketone **20** from these reactions. However, Wasserman and Liberles[10] report the formation of a small amount of **20**, in an analogous reaction, namely the photooxygenation of 2,3,4,5-tetraphenylpyrrole.

Similarly, the formation of 2,5 - dihydro - 2,3,4,5 - tetraphenylfuran (**10**), 1 - methylphenylhydroxysilyl - 1,2,3,4 - tetraphenyl - 1,3 - butadiene (**11**) and *cis, cis* - 1,2,3,4 - tetraphenyl - 1,3 - butadiene (**12**) could be explained in terms of the acid-catalyzed cleavage reactions of the starting silacyclopentadiene, **1**, as shown in Scheme 1.

In continuation of our studies, we have examined the reaction of perbenzoic acid with hexaphenylsilacyclopentadiene (**21**) which gave rise to a mixture of tetraphenylfuran (**7**) and *cis*-dibenzoylstilbene (**13**) (Scheme 1). No other characterizable products could be obtained from this run. The structures of **7** and **13** have been elucidated on the basis of spectral evidences and by comparison with authentic samples of these compounds.

In order to ascertain as to whether *cis, cis* - 1,2,3,4 - tetraphenyl - 1,3 - butadiene (**12**) is formed initially in these peracid oxidation reactions of silacyclopentadienes which might then lead to oxygenated products, the perbenzoic acid oxidation of **12** itself was carried out, under analogous experimental conditions. It is interesting to note that none of the products, **7**, **10**, **13**, **16** or **20** could be obtained from this reaction suggesting thereby that **12** is not the precursor for any of these oxidation products (Scheme 1).

We have investigated the photooxygenation reaction of a representative silacyclopentadiene with a view to finding out whether any of the products obtained from the peracid oxidation of silacyclopentadienes (Scheme 1) are formed under these conditions. Thus, the irradiation of 1 - methyl - 1 - vinyl - 2,3,4,5 - tetraphenyl - 1 - silacyclopentadiene (**22**) in cyclohexane for 4 hr under a stream of air, gave a mixture of products consisting of isodidesyl (**6**), *cis*-dibenzoylstilbene (**13**) and *trans*-dibenzoylstilbene (**23**) (Scheme 4). It may be pointed out in this connection that the same compounds, **6**, **13** and **23** also were obtained by the photooxygenation of 1,1 - dimethyl - 2,3,4,5 - tetraphenyl - 1 - silacyclopentadiene.[11]

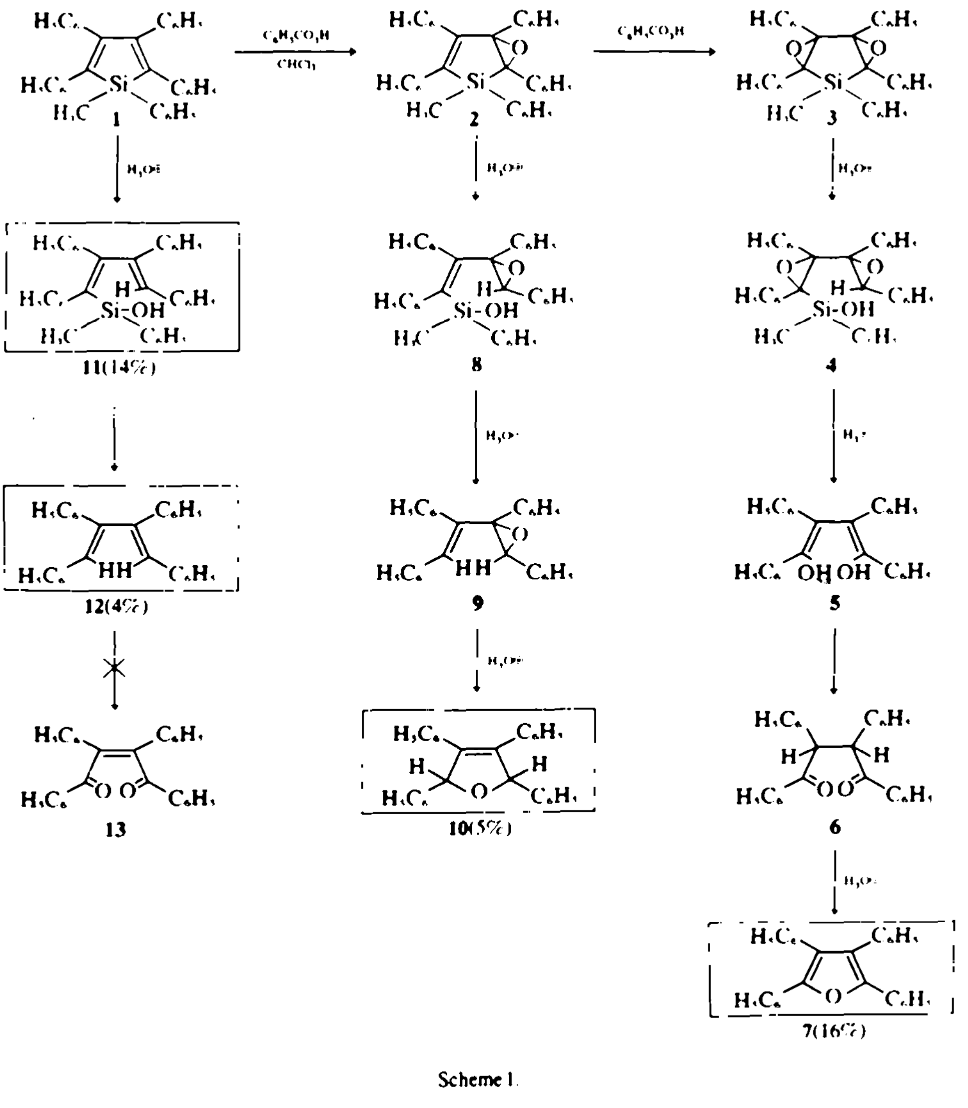
EXPERIMENTAL

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 either on a Varian T-60 or a HA-100 NMR Spectrometer using TMS as the internal standard. The mass spectra were recorded on a CEC 21-110B Mass Spectrometer.

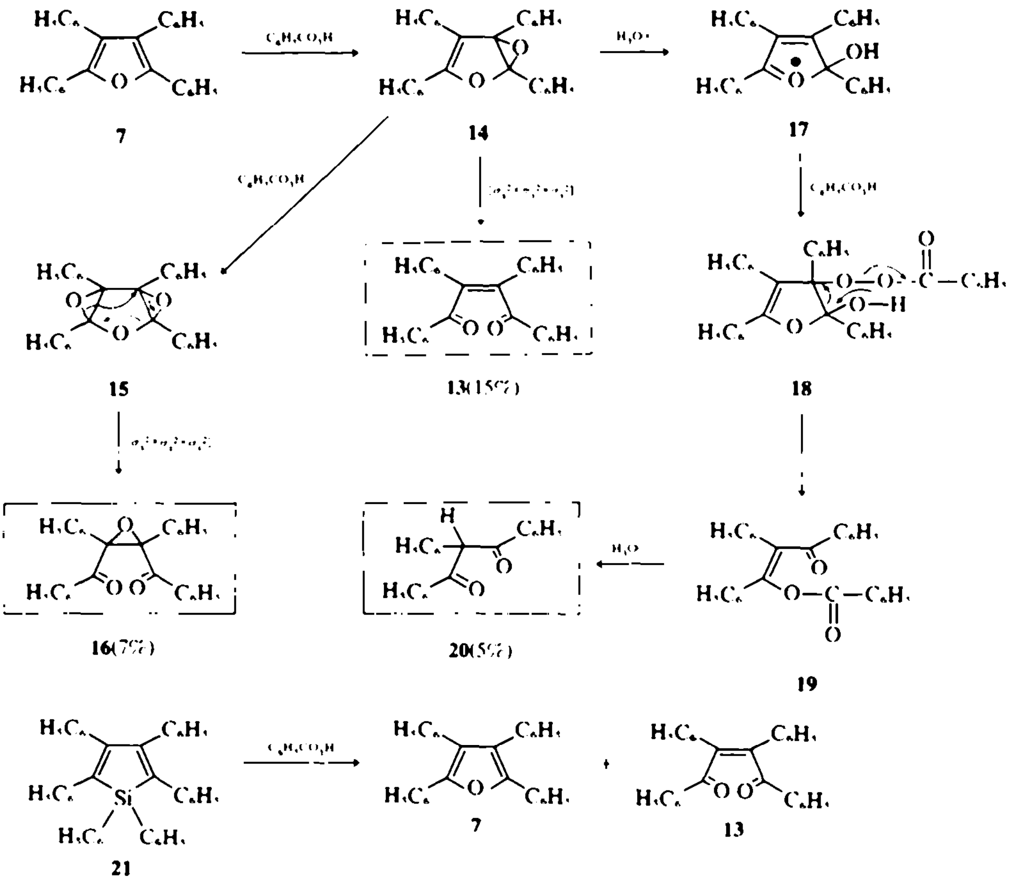
Starting materials. 1 - Methyl - 1,2,3,4,5 - pentaphenyl - 1 - silacyclopentadiene,[12] m.p. 173–174° (74%), 1 - methyl - 1 - vinyl - 2,3,4,5 - tetraphenyl - 1 - silacyclopentadiene,[12] m.p. 172–173° (55%), hexaphenylsilacyclopentadiene,[11] m.p. 190–191° (65%) and perbenzoic acid[14] were prepared by reported procedures.

Reaction of 1 - methyl - 1,2,3,4,5 - pentaphenyl - 1 - silacyclopentadiene

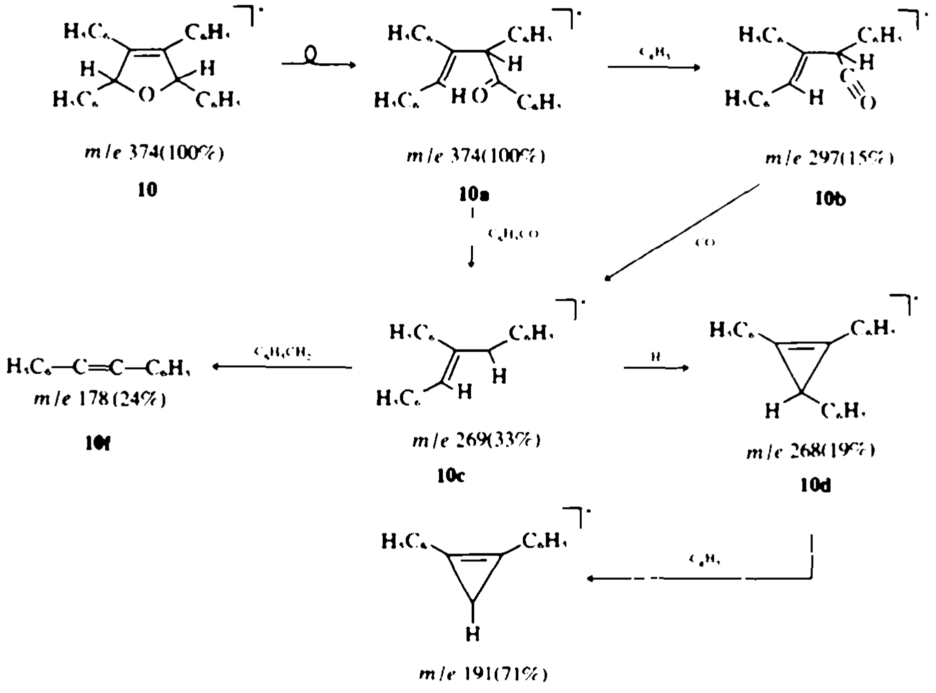
(1) *With perbenzoic acid.* A mixture of **1** (1.43 g; 3 mmol) and perbenzoic acid (0.62 g; 4.5 mmol) in 50 ml chloroform was kept at room temp for 24 hr. The mixture was washed with NaHCO$_3$aq to remove the benzoic acid and the chloroform extract was dried



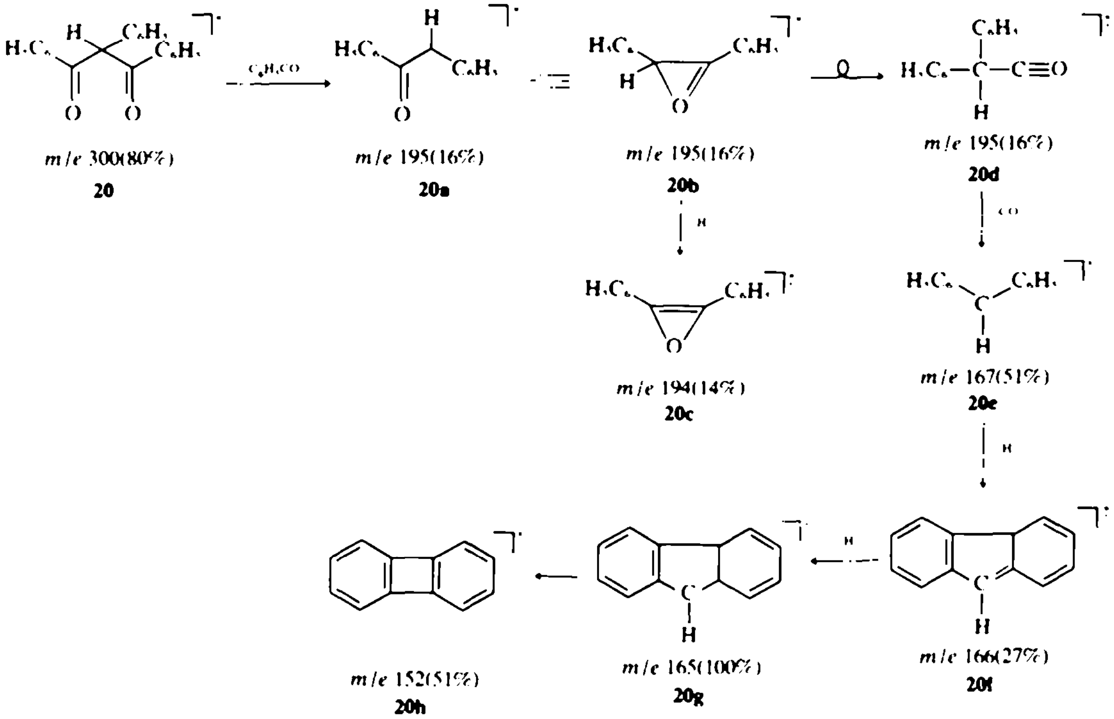
Scheme 1.



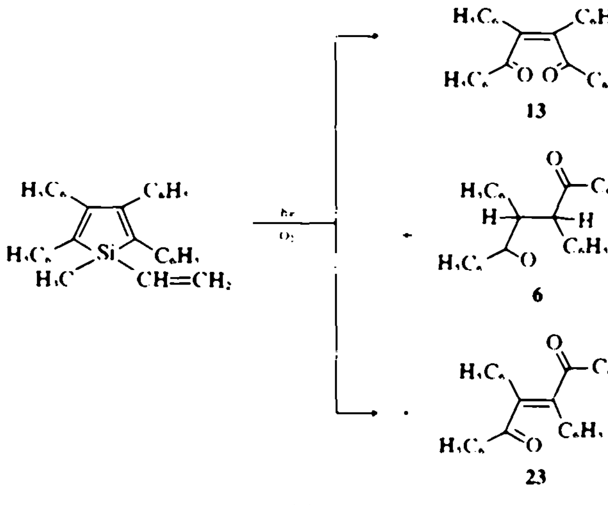
Scheme 1 (contd).



Scheme 2.



Scheme 3.



Scheme 4.

over Na_2SO_4. Removal of the solvent under vacuum gave a product mixture which was chromatographed over a silica gel column. Elution with petroleum ether (b.p. 60–80°) gave 0.17 g (16%) of 7, m.p. 173–174° after recrystallization from petroleum ether. There was no depression in the m.p. of 7 when mixed with an authentic sample.[15] Also, the IR spectrum of 7 was superimposable with that of an authentic sample.[9]

Further elution of the column with petroleum ether (b.p. 60–80°) gave 0.03 g (4%) of *cis, cis* **12**, m.p. 182–183° (m.m.p.).[14]

Elution of the column with a mixture (19:1) of petroleum ether and benzene gave 0.07 g (7%) of a product m.p. 172–173° and identified as *cis* **16** (lit.[10] m.p. 172–173°) (Found: C, 83.66; H, 5.51. $C_{28}H_{20}O_2$ requires: C, 83.17; H, 4.95%). IR spectrum (KBr) ν_{max}: 3061, 3028, 1676, 1586, 1569, 1479, 1442, 1425, 1305, 1245, 1175, 1110, 1055 and 995 cm^{-1}.

Continued elution of the column with a mixture (10:1) of petroleum ether (b.p. 60–80°) and benzene gave 0.04 g (5%) of a colorless crystalline solid, m.p. 148–149° and characterized as **20**, (lit.[7] m.p. 149°). IR spectrum (KBr) ν_{max}: 3084, 1688, 1664, 1590, 1572, 1490, 1453, 1351, 1323, 1307, 1281, 1257, 1213, 1203, 1161, 993, 988, 922, 874, 840, 818, 762, 746 and 732 cm^{-1}. UV spectrum (cyclohexane) λ_{max}: 246 (ε, 33,300), 286 (sh) (2,500), 334 (2,800) and 355 (2,700).

Further elution of the column with a mixture (4:1) of petroleum ether (b.p. 60–80°) and benzene gave 0.05 g (5%) of a colorless crystalline solid, m.p. 146–147°, which has been tentatively identified as **10** (Found: C, 89.67; H, 5.18. $C_{26}H_{22}O$ requires: C, 89.82; H, 5.88%). IR spectrum (KBr) ν_{max}: 1635, 1584, 1569, 1479, 1443, 1437, 1315, 1271, 1210, 1169, 1061, 1050, 1013, 850, 762 and 745 cm^{-1}. UV spectrum (cyclohexane) λ_{max}: 240 nm (ε, 15,400), 253 (16,400), 270 (sh) (8,700) and 346 (150). NMR spectrum ($CDCl_3$): 3.98δ (s, 2H) and 7.45δ (m, 20H).

Subsequent elution of the column with a mixture (7:3) of petroleum ether (b.p. 60–80°) and benzene gave a solid which was recrystallized from a mixture (1:1) of petroleum ether (b.p. 60–80°) and benzene to give 0.2 g (14%) of a colorless solid characterized as **11**, m.p. 158–159° (Found: C, 84.88; H, 6.30; Mol. wt., 494 (Mass spectrometry). $C_{35}H_{30}OSi$ requires: C, 85.02; H, 6.07%; Mol.wt., 494). IR spectrum (KBr) ν_{max}: 3678, 3046, 3021, 1583, 1534, 1485, 1475, 1435, 1417, 1245, 1100, 1065, 1017, 950, 912, 825, 811 and 725 cm^{-1}. UV spectrum (cyclohexane) λ_{max}: 232 nm (sh) (ϵ, 2,500), 267 (1,700), 287 (1,700) and 312 (sh) (1,100). NMR spectrum ($CDCl_3$): 0.62δ (s, 3H, Si–CH_3), 2.40δ (s, 1H, Si–OH) and 7.25δ (m, 26H, phenyl and vinyl protons).

Subsequent elution of the column with a mixture (3:2) of petroleum ether (b.p. 60–80°) and benzene gave 0.16 g (15%) of *cis* **13**, m.p. 216–217° (m.m.p.). The IR spectrum of **13** was superimposable with that of an authentic sample.[17]

Reaction of hexaphenylsilacyclopentadiene (**21**) *with perbenzoic acid*

A soln of **21** (1.35 g; 2.5 mmol) in chloroform was mixed with perbenzoic acid (0.69 g; 5 mmol) in 50 ml chloroform and was allowed to stand at room temp for 24 hr. The mixture was washed with $NaHCO_3$aq to remove the benzoic acid formed and then with cold water to remove any alkali. The organic layer was extracted with chloroform and dried over Na_2SO_4. Removal of the solvent under vacuum gave a product mixture which was chromatographed over a silica gel column. Elution of the column with petroleum ether (b.p. 60–80°) gave 0.13 g (18%) of **7**, m.p. 173–174° (m.m.p.).[15]

Further elution of the column with a mixture (9:1) of petroleum ether (b.p. 60–80°) and benzene gave 0.19 g of an unidentified product m.p. 219–220° (Found: C, 84.30; H, 5.30; Mol. wt., 466 (Mass spectrometry). $C_{33}H_{26}OSi$ requires: C, 84.98; H, 5.58%; Mol. wt., 466). IR spectrum (KBr) ν_{max}: 3052, 3032, 1694, 1584, 1566, 1496, 1478, 1436, 1422, 1234, 1194, 1164, 1138, 1128, 1076, 1040, 1020, 1012, 974, 920, 904, 882, 846, 796, 788, 775, 764, 756, 748, 740, 728 and 708 cm^{-1}. UV spectrum (cyclohexane) λ_{max}: 233 nm (ϵ, 3,800), 252 (3,300), 330 (190) and 339 (150). NMR spectrum ($CDCl_3$): 1.96δ (s, 1H) and 7.50δ (m, 20H).

Further elution of the column with a mixture (5:1) of petroleum ether (b.p. 60–80°) and benzene gave 0.1 g (13%) of *cis* **13**, m.p. 217–218° (m.m.p.).[17]

Reaction of cis,cis *- 1,2,3,4 - tetraphenyl - 1,3 - butadiene* (**12**) *with perbenzoic acid*

To a soln of **12** (0.65 g; 1.8 mmol) in 20 ml chloroform perbenzoic acid (0.38 g; 2.7 mmol) was added and the mixture was kept at room temp for 24 hr. Work-up of the mixture as in the earlier cases and chromatography of the mixture gave 0.62 g (96%) of a product m.p. 161–162° and isomeric with the starting tetraphenylbutadiene (Found: C, 94.04; H, 5.90; Mol. wt., 358 (Mass spectrometry). $C_{28}H_{22}$ requires: C, 93.90; H, 6.10%; Mol. wt., 358). IR spectrum (KBr) ν_{max}: 3058, 3026, 1582, 1481, 1455, 1437, 1061, 1017, 989, 918, 862, 772, 762, 746, 726 and 690 cm^{-1}. UV spectrum (cyclohexane) λ_{max}: 231 nm (ϵ, 1,500), 306 (1,500), 320 (1,600) and 332 (1,700). NMR spectrum ($CDCl_3$): 6.65δ (m, 22H, phenyl and vinyl protons).

Irradiation of 1 - methyl - 1 - vinyl - 2,3,4,5 - tetraphenyl - 1 - silacyclopentadiene **22**

A soln of **22** (1.8 g; 4.25 mmol) in cyclohexane was photolysed using a 450 W-Hanovia medium-pressure mercury lamp for 4 hr. Removal of the solvent under vacuum gave a residue which was chromatographed over neutral alumina. Elution with a mixture (19:1) of petroleum ether (b.p. 60–80°) and benzene gave 0.1 g (6%) of a compound, m.p. 229–230° and characterized as *trans* **23**. There was no depression in the m.p. of **23**, when mixed with an authentic sample.[15] Also, the IR spectrum of **23** was superimposable with that of an authentic sample.

Continued elution of the column with the same mixture of solvents yielded 0.12 g (7%) of a colorless solid identified as **6**, m.p. 159° (lit.[11] m.p. 160–161°).

Further elution of the column with a mixture (9:1) of petroleum ether (b.p. 60–80°) and benzene gave 0.5 g (33%) of *cis* **13**, m.p. 215–216° (m.m.p.).[17] Subsequent elution of the column with solvents of higher polarity did not give any identifiable products.

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