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PHOTOCHEMICAL AND THERMAL TRANSFORMATIONS OF 7-SILABICYCLO[2.2.1]HEPTADIENE AND 7-SILABICYCLO[2.2.1]HEPTENE SYSTEMS

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Summary

2,3-Dicarbomethoxy-7,7-dimethyl-7-silabicyclo[2.2.1]hepta-2,5-diene (III) on photolysis gave dimethyl tetraphenylphthalate whereas the photolysis of 7,7-dimethyl-7-silabicyclo[2.2.1]hep-5-ene-2,3-dicarboxylic anhydride (XIa) resulted in the formation of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (XIIIa). The thermolysis of XIa also gave rise to XIIIa. Similarly, the photolysis as well as thermolysis of 1,4,5,6,7,7-hexaphenyl-7-silabicyclo[2.2.1]-hept-5-ene-2,3-dicarboxylic anhydride (XIb) led to hexaphenylsilacyclopentadiene (XIIIb). Attempts to detect radical intermediates in these thermal and photochemical transformations by carrying out the reaction in the presence of hydroquinone, hydrazobenzene, 3,6-diphenyl-1,2-dihydro-1,2,4,5-tetrazine, cumene and tolan were unsuccessful. An attempted preparation of 7-silabicyclo[2.2.1]hepta-2,5-dienes by the reaction of silacyclopentadienes such as 1-methyl-1-vinyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (XV) and 1-methyl-1,2,3,4,5-pentaphenyl-1-silacyclopentadiene (XVI) with dimethyl acetylenedicarboxylate resulted in the isolation of dimethyl tetraphenylphthalate indicating that the corresponding 7-silabicyclo[2.2.1]hepta-2,5-dienes are thermally unstable.

Introduction

Studies on thermal fragmentation of several suitably substituted norbornadiene derivatives are reported to give benzene derivatives [1-4]. Similarly, cycloeliminations of carbenes are well documented [1]. Thermal decompositions of several heterosubstituted norbornadienes have been examined by different groups of workers, and the loss of dimethylsilylene [5,6], diphenylsilylene [7] and dimethylgermylene [8,9], as well as C_6H_5P [10-12] and C_6H_5As [13] has been reported.

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Of particular interest to us is the thermal fragmentation of 7-silabicyclo[2.2.1]heptadienes and 7-silabicyclo[2.2.1]heptenes. The thermal decomposition of a 7-silabicyclo[2.2.1]heptadiene such as 2,3-benzo-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silabicyclo[2.2.1]hepta-2,5-diene (I) is known to give 1,2,3,4-tetraphenylnaphthalene (II) in 88% yield and an amorphous dimethylsilyl polymer [5]. Similarly, 2,3-dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silabicyclo[2.2.1]hepta-2,5-diene (III) [5] and 7,7-dimethyl-1,2,3,4,5-pentaphenyl-7-silabicyclo[2.2.1]hepta-2,5-diene (IV) [5] on pyrolysis have been reported to give the corresponding benzene derivatives.

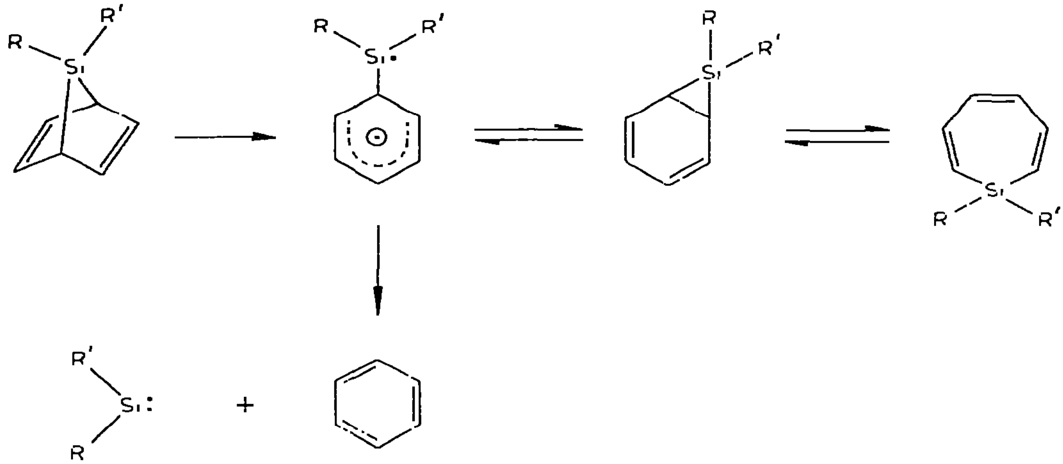
Barton and coworkers [14] have examined the thermal decomposition of 1,4-diphenyl-2,3-bis(trifluoromethyl)-7,7-dimethyl-7-silabicyclo[2.2.1]hepta-2,5-diene (V) and shown that 1,1,2,2-tetrafluoro-3,6-diphenylbenzocyclobutene (VI) and dimethyldifluorosilane (VII) were obtained. They have also shown that photolysis of V resulted in the formation of 2,3-bis(trifluoromethyl)-1,4-diphenylbenzene (VIII). Similar thermal decomposition studies on IV and V have been reported quite recently by Maruca and coworkers [15].

The thermal decomposition of a 7-silabicyclo[2.2.1]heptadiene derivative may proceed either through a symmetry-allowed, linear cheletropic reaction [16] or through a multistep pathway involving radical intermediates as shown in Scheme 1.

Results and discussion

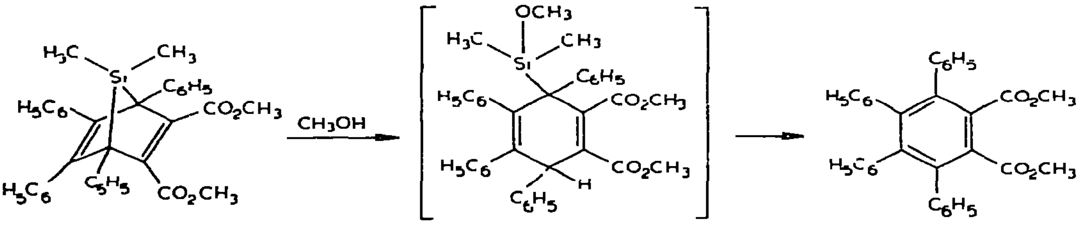
The object of the present investigation was to examine the photochemical and thermal transformations of a few representative 7-silabicyclo[2.2.1]heptadienes and 7-silabicyclo[2.2.1]heptenes with a view to examining the details of the fragmentation processes. The thermal decomposition of 2,3-dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silabicyclo[2.2.1]hepta-2,5-diene III has been reported earlier by Gilman and coworkers [5] to give dimethyl-1,2,3,4-tetraphenylphthalate (IX). During the course of the present investigations, we examined the photochemical transformations of III. The photolysis of III in benzene gave IX in 88% yield. It has been observed that when III was refluxed in benzene in the absence of light for even 10 h it resulted in nearly 94% recovery of unchanged starting material, indicating that the decomposition is truly accelerated under photochemical conditions. A probable mode of transformation of III into IX would involve a symmetry-allowed loss of a dimethylsilylene moiety or a stepwise process involving a radical intermediate (Scheme 1). A second possible mode of reaction would involve a 1,3-sigmatropic shift of the silylene moiety to give silacycloheptatriene derivatives which can valence isomerize to give products like the silanorcaradienes (Scheme 1). With a view to ascertaining whether any radical intermediates are formed in these reactions, we have examined the photolysis of III in the presence of radical traps such as hydroquinone, hydrazobenzene, 3,6-diphenyl-1,2-dihydro-1,2,4,5-tetrazine and cumene. Thus when III was irradiated in the presence of an excess of hydroquinone in benzene under nitrogen atmosphere, dimethyl-1,2,3,4-tetraphenylphthalate (IX) was obtained in 50% yield. Nearly all of the hydroquinone (94%) was isolated unchanged. Similarly, irradiation of III in the presence of hydrazobenzene gave IX in 40% yield and azobenzene in 81%

SCHEME 1



yield. The formation of azobenzene is attributed to the photochemical oxidation of hydrazobenzene, as was shown in a blank experiment. Likewise, when the irradiation of III was carried out in the presence of 3,6-diphenyl-1,2-dihydro-1,2,4,5-tetrazine, IX was obtained in 80% yield, together with 3,6-diphenyl-1,2,4,5-tetrazine and 50% of unchanged 3,6-diphenyl-1,2-dihydro-1,2,4,5-tetrazine. Also, when the irradiation of III was carried out in the presence of cumene, dimethyl 1,2,3,4-tetraphenylphthalate (IX) was the only isolable product. In none of these cases, could we isolate dimethyl 1,4-dihydro-1,2,3,4-tetraphenylphthalate (X) or its precursor, which would be expected under these conditions. Further, it has also been observed that the photo-reactions of III are not retarded in the presence of reagents like hydroquinone, hydrazobenzene 3,6-diphenyl-1,2-dihydro-1,2,4,5-tetrazine and cumene, which can act as radical traps. From these experiments, we conclude that the decomposition of III may in all probability be going through a non-radical pathway.

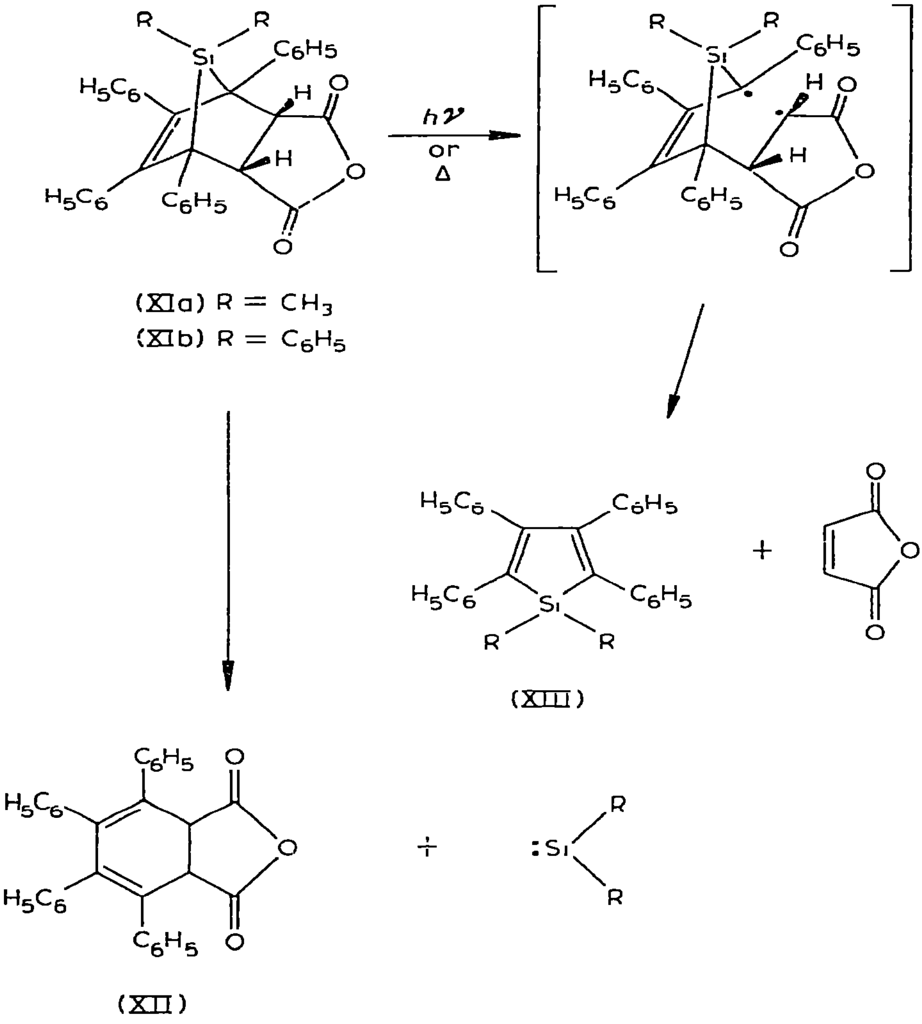
In this connection, 7-silabicyclo[2.2.1]hepta-2,5-diene systems undergo hydrolytic cleavage to give benzene derivatives [5,7,15,17-19]. We have observed, during the course of these investigations, that when 2,3-dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silabicyclo[2.2.1]hepta-2,5-diene (III) was refluxed in methanol, dimethyl 1,2,3,4-tetraphenylphthalate (IX) was obtained in 90% yield. The most probable pathway for this reaction involves nucleophilic attack at silicon by methanol followed by loss of the silicon moiety (eqn. 1).



(III) (IX) (1)

With a 7-silabicyclo[2.2.1]heptene system (XI), the photochemical transformation can proceed through different possible pathways as shown in Scheme 2. One of these would involve a concerted or stepwise loss of the silylene moiety

SCHEME 2



to give dihydrotetraphenylphthalic anhydride (XII). Another mode would be a Retro-Diels—Alder type of reaction leading to the formation of the parent silacyclopentadiene XIII and maleic anhydride.

We have examined the thermal decomposition of 7,7-dimethyl-1,4,5,6-tetraphenyl-7-silabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (XIa) and 7,7-diphenyl-7-silabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (XIb). The themolysis of XIa at ca. 200° gave a 74% yield of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (XIIIa). A small amount of maleic anhydride (12%) was also isolated from this run. Similarly, the thermolysis of XIb at ca. 340° gave hexaphenylsilacyclopentadiene XIIIb in a 80% yield. With a view to trapping the dimethylsilylene species, if formed, we have examined the thermolysis of XIa in the presence of tolan. However, only the starting material was recovered in 90% yield and no 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexadiene (XIV) was obtained.

Thus, the formation of XIIIa and XIIIb in the thermolysis of XIa and XIb, respectively, would strongly suggest that the major pathway for the decomposition of these compounds is through a symmetry allowed $\sigma^2 s + \pi^2 s + \sigma^2 s$ fragmentation (Retro-Diels—Alder reaction)[20].

We have also attempted the photochemical decomposition of XIa and XIb. Thus, on irradiation in benzene solution, XIa gave 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (XIIa) in 85% yield. No reaction, however, was observed when XIa was refluxed in benzene for 6 h in the absence of any light source.

The photolysis of XIb in benzene gave rise to XIIIb in a 70% yield. Here again no reaction was observed when XIb was refluxed in benzene for 4 h in the absence of light.

The fact that the 7-silabicyclo[2.2.1]heptenes, XIa and XIb, under photochemical conditions give rise to the parent silacyclopentadienes, XIIIa and XIIIb, respectively, would suggest that the most favored pathway for the reaction is perhaps to go through a radical intermediate as shown in Scheme 2.

Finally we report the attempted reaction of 1-methyl-1-vinyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (XV) and 1-methyl-1,2,3,4,5-pentaphenyl-1-silacyclopentadiene (XVI), respectively, with dimethyl acetylenedicarboxylate. When XV was heated with dimethyl acetylenedicarboxylate, dimethyl 1,2,3,4-tetraphenylphthalate (IX) was obtained in 90% yield. The formation of IX would suggest that the initially formed 7-silabicyclo[2.2.1]hepta-2,5-diene undergoes facile fragmentation under the reaction conditions. Similarly, XVI on treatment with dimethyl acetylenedicarboxylate gave IX in a 92% yield.

From our studies, we find that the thermal decomposition of 7-silabicyclo-[2.2.1]heptadienes proceeds relatively faster than the corresponding 7-silabicyclo[2.2.1]heptenes. With 7-silabicyclo[2.2.1]heptenes, the most favored pathway seems to involve carbon—carbon bond cleavage leading to the parent silacyclopentadienes and not to elimination of the silylene moiety.

Experimental

All melting points are uncorrected. The IR spectra were recorded on a Perkin—Elmer Model 521 Infrared Spectrometer. Solvents were dried over sodium and freshly distilled before use. The irradiation experiments were carried out in a pure and dry nitrogen atmosphere using either a Hanovia 450 W medium pressure mercury lamp or a Griffin—Srinivasan 150 W Rayonet Reactor, and the solutions were degassed before irradiation.

Starting materials

2,3-Dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silabicyclo[2.2.1]-hepta-2,5-diene (III), m.p. 195-196° (dec.) (85%) [5], 7,7-dimethyl-1,4,5,6-tetraphenyl-7-silabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (XIa), m.p. 237-238° (72%) [21], 1,4,5,6,7,7-hexaphenyl-7-silabicyclo[2.2.1]hept-5-ene-

2,3-dicarboxylic anhydride (XIb), m.p. 225-226° (83%) [7], 1-methyl-1-vinyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (XV), m.p. 177-178° (55%) [21] and 1-methyl-1,2,3,4,5-pentaphenyl-1-silacyclopentadiene (XVI), m.p. 173-174° (74%) [21] were prepared by reported procedures.

Photolysis of 2,3-dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silabicyclo[2.2.1]hepta-2,5-diene (III)

A solution of 0.28 g (0.5 mmol) of III in 150 ml of benzene was photolysed for 5 h. Removal of the solvent gave a product which was recrystallized from a mixture (1/3) of petroleum ether (b.p. 60-80°) and benzene to give 0.22 g (88%) of dimethyl 1,2,3,4-tetraphenylphthalate IX, m.p. 256-257° (mixture m.p.). The IR spectra of IX was superimposable on that of an authentic sample [7].

In a blank run, a solution of 0.28 g (0.5 mmol) of III in 150 ml of benzene was refluxed for 10 h. Removal of the solvent and work-up in the usual manner gave 0.26 g (94%) of the unchanged starting material III, m.p. 195-196° (dec.) (mixture m.p.) [5].

Photolysis of 2,3-dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silabicyclo[2.2.1]hepta-2,5-diene (III) in presence of hydroquinone

A mixture of 0.28 g (0.5 mmol) of III and 0.16 g (1.5 mmol) of hydroquinone was irradiated in benzene for 5 h. After the irradiation, an insoluble colorless solid (0.1 g, 63%, m.p. and mixture m.p. 172-173°) was left behind, which was characterized as hydroquinone. The clear supernatant liquid was concentrated under vacuum and the residue chromatographed over a neutral alumina column. On concentration of the benzene fraction, a colorless solid (0.13 g, 50%) was obtained, which was characterized as dimethyl 1,2,3,4-tetraphenylphthalate (IX) [7], m.p. and mixture m.p. 255-256°. On evaporation of the ethyl acetate fraction, a colorless solid (0.05 g, 31%) was obtained which was characterized as hydroquinone, m.p. and mixture m.p. 172-173°.

Photolysis of 2,3-dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silabicyclo[2.2.1]hepta-2,5-diene (III) in presence of hydrazobenzene

A mixture of 0.28 g (0.5 mmol) of III and 0.28 g (1.5 mmol) of hydrazobenzene was photolyzed in dry cyclohexane for 7 h. Removal of the solvent under vacuum and chromatography over neutral alumina gave 0.22 g (81%) of azobenzene, m.p. and mixture m.p. 67-68°. Elution of the column with benzene and subsequent removal of the solvent gave 0.1 g (40%) of dimethyl 1,2,-3,4,-tetraphenylphthalate, m.p. and mixture m.p. 256-257° [7]. Continued elution of the column with acetone and concentration gave 0.04 g (14%, m.p. > 400°) of a polymeric material whose IR spectrum (KBr) showed bands due to $Si{-}CH_3$ [$\nu(Si{-}CH_3)$ 1250, 840 cm^{-1}].

In a blank experiment, a cyclohexane solution of 0.28 g (1.5 mmol) of hydrazobenzene was irradiated for 7 h. Removal of the solvent under vacuum and chromatography over a neutral alumina column gave 0.24 g (88%) of azobenzene, m.p. and mixture m.p. 67-68°.

Photolysis of 2,3-dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silabicyclo[2.2.1]hepta-2,5-diene (III) in presence of 3,6-diphenyl-1,2-dihydro-1,2,4,5-tetrazine

A solution of 0.56 g (1 mmol) of III and 0.36 g (1.5 mmol) of 3,6-diphenyl-1,2-dihydro-1,2,4,5-tetrazine in 150 ml of dry, thiophene-free benzene was irradiated for 5 h. Removal of the solvent under vacuum and chromatography over a neutral alumina column gave a pink crystalline solid (0.13 g, 37%) which was characterized as 3,6-diphenyl-1,2,4,5-tetrazine, m.p. and mixture m.p. 189-190° [22]. Evaporation of the benzene fraction gave 0.19 g (54%) of 3,6-diphenyl-1,2-dihydro-1,2,4,5-tetrazine, m.p. and mixture m.p. 184-185° [22]. Concentration of a further fraction of benzene gave 0.42 g (84%) of dimethyl 1,2,3,4-tetraphenylphthalate (IX), m.p. and mixture m.p. 256-257° [7]. The evaporation of the methanol fraction of the column gave 0.08 g (14%) of a polymeric material, the IR spectrum (KBr) of which showed bands characteristic of Si—CH_3.

Photolysis of 2,3-dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silabicyclo[2.2.1]hepta-2,5-diene (III) in presence of cumene

A solution of 0.56 g (1 mmol) of III and 0.4 g (3.5 mmol) of cumene in 175 ml of dry, freshly distilled cyclohexane was irradiated for 7 h. Removal of the solvent under vacuum and chromatography over a neutral alumina column gave 0.1 g (20%) of dimethyl 1,2,3,4-tetraphenylphthalate (IX) [7].

Photolysis of 7,7-dimethyl-1,4,5,6-tetraphenyl-7-silabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (XIa)

0.52 g (1 mmol) of XIa was dissolved in 200 ml of thiophene-free benzene and photolysed for 2½ h. Removal of the solvent under vacuum gave a yellow solid which on recrystallization from petroleum ether (b.p. 60-80°) gave 0.35 g (85%) of 1,1-dimethyl-2,3,4,5-tetraphenylsilacyclopentadiene (XIIIa), m.p. 180-181° (mixture m.p.) [5].

In a blank experiment, a benzene solution of 0.26 g (0.5 mmol) of XIa was refluxed for 6 h. Removal of the solvent gave a colorless solid which on usual work-up gave 0.25 g (96%) of the starting material (XIa), m.p. 236-237° (mixture m.p.) [21].

Photolysis of 1,4,5,6,7,7-hexaphenyl-7-silabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (XIb)

A benzene solution of 0.32 g (0.5 mmol) of XIb was photolysed for 3 h. On removal of the solvent and usual work-up, 0.19 g (70%) of hexaphenylsilacyclopentadiene (XIIIb), m.p. and mixture m.p. 190-191° [7] was obtained.

In a blank experiment, a benzene solution of 0.32 g (0.5 mmol) of XIb was refluxed for 4 h and then the solvent removed under vacuum to give 0.31 g (97%) of unchanged starting material, XIb, m.p. and mixture m.p. 225-226° [7].

Reaction of 1-methyl-1-vinyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (XV) with dimethyl acetylenedicarboxylate

A mixture of 0.22 g (0.5 mmol) of XV and 0.49 g (3.5 mmol) of dimethyl acetylenedicarboxylate was heated at ca. 70° in an oil bath for 4 h. The reaction mixture was finally washed thrice with 10 ml portions of petroleum ether (b.p. 60-80°) each time to remove any unreacted acetylenic ester. A pale yellow solid was left behind, yield 0.26 g (90%), which melted at ca. 253-255°, which was recrystallized from a mixture (1/3) of petroleum ether (b.p. 60-80°) and benzene to give 0.24 g (85%) of dimethyl 1,2,3,4-tetraphenylphthalate (IX), m.p. and mixture m.p. 256-257° [7].

Reaction of 1-methyl-1,2,3,4,5-pentaphenyl-1-silacyclopentadiene (XVI) with dimethyl acetylenedicarboxylate

A mixture of 0.24 g (0.5 mmol) of XVI and 0.22 g (1.5 mmol) of dimethyl acetylenedicarboxylate was heated at ca. 70° in an oil bath for 10 h. The reaction mixture was washed thrice with 10 ml portions of petroleum ether (b.p. 60-80°) each time to remove any unreacted acetylenic ester. A pale yellow solid was obtained which was recrystallized from a mixture (1/3) of petroleum ether (b.p. 60-80°) and benzene to give 0.28 g (90%) of dimethyl 1,2,3,4-tetraphenylphthalate (IX), m.p. and mixture m.p. 256-257° [7].

In a repeat experiment, 0.24 g (0.5 mmol) of XVI and 0.2 g (1.4 mmol) of dimethyl acetylenedicarboxlate were heated at ca. 50° for 24 h to give 0.27 g (87%) of dimethyl 1,2,3,4-tetraphenylphthalate (IX).

In another repeat experiment, a mixture of 0.24 g (0.5 mmol) of XVI and 0.5 g (3.5 mmol) of dimethyl acetylenedicarboxylate was heated at ca. 60° for 11 h to give 0.26 g (85%) of IX.

Thermolysis of 7,7-dimethyl-1,4,5,6-tetraphenyl-7-silabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (XIa)

0.52 g (1 mmol) of XIa was thermolysed in a sealed tube at ca. 200° for 4 h. The reaction mixture was then triturated with petroleum ether (b.p. 60-80°) to yield a pale yellow solid which was recrystallized from petroleum ether (b.p. 60-80°) to yield 0.38 g (74%) of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (XIIIa), m.p. and mixture m.p. 179-180° [5]. On concentration of the mother liquor with small amounts of benzene, 0.06 g (12%) of maleic anhydride, m.p. and mixture m.p. 52-53°, was obtained.

Thermolysis of 7,7-dimethyl-1,4,5,6-tetraphenyl-7-silabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (XIa) with tolan

A mixture of 0.13 g (0.25 mmol) of XIa and 0.18 g (1 mmol) of tolan was heated in a sealed tube in an oil bath at ca. 140° for 20 h. Then the reaction mixture was triturated with petroleum ether (b.p. 60-80°) to yield 0.12 g (89%) of unchanged starting material, XIa, m.p. and mixture m.p. 235-237° [21].

Thermolysis of 1,4,5,6,7,7-hexaphenyl-7-silabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (XIb)

0.44 g (0.67 mmol) of XIb was heated in a sealed tube at ca. 340° for 4 h in a Sargent Bomb. The reaction mixture was chromatographed over a neutral alumina column and the solvent from the petroleum ether (b.p. 60-80°) fraction was removed under vacuum to give 0.28 g (80%) of hexaphenylsilacyclopentadiene (XIIIb), m.p. and mixture m.p. 190-191° [7].

Thermolysis of 2,3-dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silabicyclo[2.2.1]hepta-2,5-diene (III) in presence of methanol

A methanol solution of 0.28 g (0.5 mmol) of III was refluxed for 7 h and then the solvent was removed under vacuum. A colorless solid was obtained which on careful crystallization from a mixture (1/3) of petroleum ether (b.p. 60-80°) and benzene gave 0.23 g (90%) of dimethyl 1,2,3,4-tetraphenylphthalate (IX), m.p. and mixture m.p. 256-257° [7].

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