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ALKALI METAL, ALKALINE AND ACIDIC DECOMPOSITION OF SILACYCLOPENTADIENES

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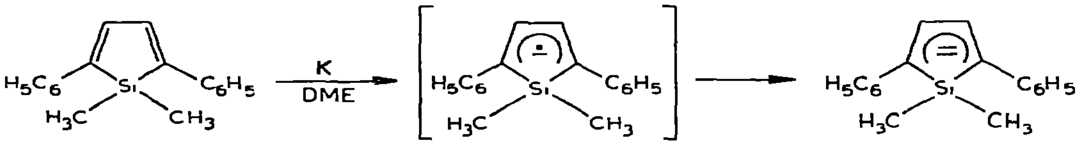
Summary

1,1-Dimethyl-2,5-diphenyl-1-silacyclopentadiene and 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (X) are cleaved by sodium hydroxide as well as by hydrochloric acid to give *trans, trans*-1,4-diphenylbutadiene and *cis,cis*-1,2,3,4-tetraphenylbutadiene, respectively. Compound X, hexaphenylsilacyclopentadiene and 1-methyl-1,2,3,4,5-pentaphenyl-1-silacyclopentadiene, on treatment with potassium in 1,2-dimethoxyethane gave intensely red colored dianions which on quenching in moist tetrahydrofuran gave rise to α,α'-dibenzylstilbene. A pathway for the reaction is suggested.

Introduction

There exists a brief report [1] that silacyclopentadiene (I) reacts with potassium sand in tetrahydrofuran to give the corresponding anion (II). Treatment of II with excess of bromobenzene yielded a mixture of 1-phenylsilacyclopentadiene (III) and 1,1-diphenylsilacyclopentadiene (IV). Janzen and co-workers [2] have reported that 1,1-dimethyl-2,5-diphenylsilacyclopentadiene (V) on treatment with sodium or potassium in 1,2-dimethoxyethane (DME) gave the corresponding anion radical (VI) followed by the dianion (VII) (eqn. 1).



(V) (VI) (VII) (1)

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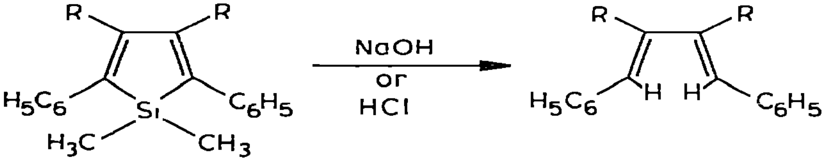
Similarly, 1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (VIII), 1,2,3,4,5-pentaphenyl-1-silacyclopentadiene (IX) and 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (X) [2, 3] have been reported to form the corresponding anion radicals followed by the dianions on treatment with potassium in tetrahydrofuran or DME. Electrochemical reduction of hexaphenylsilacyclopentadiene (XI) has been reported [4] to give the corresponding anion radical and the dianion. Similarly, some heterocyclopentadienes like hexaphenylgermacyclopentadiene (XII), 1,1-dimethyl-2,3,4,5-tetraphenyl-1-stannacyclopentadiene (XIII), pentaphenylphosphole (XIV), pentaphenylarsole (XV) and pentaphenyl-1-boracyclopentadiene (XVI) are reported [4] to give the corresponding anion radicals and dianions, on reduction with potassium in DME.

The object of the present investigation has been to examine the nature of the products formed in the alkaline and alkali metal cleavage of some representative silacyclopentadienes as well as their decomposition by acid.

Results and discussion

1,1-Dimethyl-2,5-diphenyl-1-silacyclopentadiene (V), on refluxing with sodium hydroxide in DME, gave a product identified as *trans,trans*-1,4-diphenylbutadiene (XVII) in a 75% yield. An amorphous polymeric material containing silicon was also obtained in this run. Similarly, 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (X) on treatment with sodium hydroxide gave a product identified as *cis,cis*-1,2,3,4-tetraphenylbutadiene (XVIII) in a 88% yield, together with a polymer. When X was refluxed in DME with sodium hydroxide, XVIII was obtained in a 85% yield in 2 h (eqn. 2). The formation of *trans,trans*-1,4-diphenylbutadiene (XVII) and *cis,cis*-1,2,3,4-tetraphenylbutadiene (XVIII) would strongly suggest that the reaction is proceeding by nucleophilic attack of the hydroxide ion on silicon and consequent ring opening retaining the geometry of the parent silacyclopentadienes.



(2)

(V), R = H

(X), R = C_6H_5

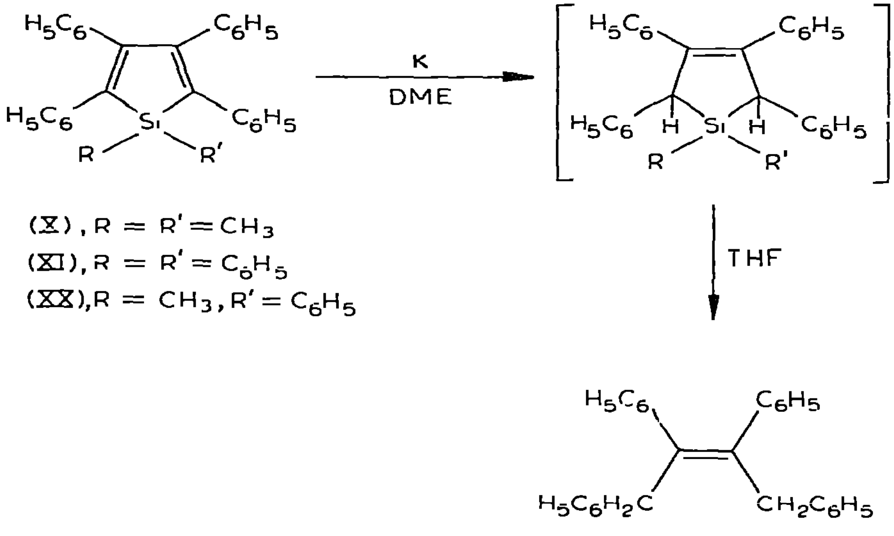
(XVII), R = H

(XVIII), R = C_6H_5

In this connection, we also report that 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (V) on refluxing in DME with concentrated hydrochloric acid gave XVII in a 80% yield. Similarly, 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (X) on treatment with hydrochloric acid gave XVIII in a 85% yield (eqn. 2). It should be noted that Freedman reported [5] that 1,1-dimethyl-2,3,4,5-tetraphenyl-1-stannacyclopentadiene (XIII) on brief exposure to a dilute solution of acetic acid in alcohol undergoes rapid cleavage of the unsaturated ring-carbon—tin bonds with the quantitative formation of *cis,cis*-1,2,3,4-tetraphenylbutadiene (XVIII).

With a view to finding the nature of the products formed on treatment of silacyclopentadienes with potassium, we have studied the reaction of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (X). When X was shaken vigorously with freshly cut potassium metal in DME, it gave an intense blue color; on prolonged shaking, a deep red color was seen in the solution which is due to the formation of the dianion [2]. This dianion on treatment with moist tetrahydrofuran gave α,α′-dibenzylstilbene (XIX) [6] in a 65% yield (eqn. 3).

Similarly, hexaphenylsilacyclopentadiene (XI) on treatment with potassium in 1,2-dimethoxyethane gave a deep red colored solution of the corresponding dianion which on treatment with moist tetrahydrofuran gave α,α′-dibenzylstilbene (XIX) [6] in a 70% yield (Eqn. 3).



(X), $R = R' = CH_3$
(XI), $R = R' = C_6H_5$
(XX), $R = CH_3, R' = C_6H_5$

(3)

(XIX)

On the same lines as above, 1-methyl-1,2,3,4,5-pentaphenyl-1-silacyclopentadiene (XX) [7] on reduction with potassium in DME gave an intense red colored dianion solution which on treatment with moist tetrahydrofuran gave a 70% yield of α,α′-dibenzylstilbene (XIX) [6] (eqn. 3).

The fact that *cis*-α,α′-dibenzylstilbene is formed in these alkali metal cleavages of silacyclopentadienes suggests that the dihydro derivative formed (eqn. 3) is undergoing solvolysis with the loss of the silicon moiety as against the initial loss of the silicon moiety followed by solvolysis which would be expected to give *cis,cis*-tetraphenylbutadiene (XVIII). In this connection, Doran and Waack [12] have reported that *cis,cis*-tetraphenylbutadiene (XVIII) on treatment with lithium or sodium in tetrahydrofuran isomerises to *trans,-trans*-tetraphenylbutadiene (XXI) in a 70% yield. Our attempts to isolate either XVIII or XXI from the above runs were unsuccessful, proving thereby that the reaction occurs via a dihydro derivative which undergoes solvolysis to give XIX.

Experimental

All melting points are uncorrected. The IR spectra were recorded on a Perkin—Elmer Model 521 Infrared Spectrometer and electronic spectra on a Beckman DU Spectrophotometer. NMR traces were recorded on a Varian HA-100 Spectrometer using tetramethylsilane as the internal standard.

Starting materials

1,1-Dimethyl-2,5-diphenyl-1-silacyclopentadiene (V), m.p. 132-133° (65%) [8], 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (X), m.p. 180-181° (65%) [9], 1-methyl-1,2,3,4,5-pentaphenyl-1-silacyclopentadiene (XX), m.p. 173-174° (74%) [7] and hexaphenylsilacyclopentadiene (XI), m.p. 190-191° (65%) [10] were prepared by reported procedures. 1,2-Dimethoxyethane (DME) was distilled over sodium before use.

Reaction of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (V) with alkali

A solution of 0.13 g (0.5 mmol) of V in 50 ml of DME with 0.8 g (20 mmol) of sodium hydroxide was refluxed for 10 h. After neutralising the alkali, the solution was extracted with benzene and evaporated to give 0.09 g of a colorless solid which was recrystallised from a mixture (1/4) of benzene and ethyl alcohol to yield 0.08 g (75%) of a product identified as *trans,trans*-1,4-diphenylbutadiene (XVII), m.p. and mixture m.p. 152-153° [11]. The benzene-insoluble portion weighed 0.02 g (15%), m.p. > 400° and had IR bands characteristic of $SiCH_3$ [$\nu(SiCH_3)$ 1240, 840 cm^{-1}].

Reaction of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (X) with alkali at room temperature

A solution of 0.21 g (0.5 mmol) of X in 50 ml of DME with 0.4 g (10 mmol) of sodium hydroxide was allowed to stand at room temperature for 48 h. The yellow color of the solution faded slowly. The reaction mixture was washed with water repeatedly to remove all the alkali and finally with benzene. The benzene extract was concentrated under vacuum. A pale yellow solid was obtained which on warming with benzene left an insoluble colorless solid (0.03 g, m.p. > 400°), the IR spectrum (KBr) of which showed bands characteristic of $SiCH_3$ grouping.

The benzene-soluble portion was evaporated to give 0.15 g (80%) of a product identified as *cis,cis*-1,2,3,4-tetraphenylbutadiene (XVIII), m.p. and mixture m.p. 183-184° [5].

Reaction of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (X) in presence of alkali under refluxing conditions

A solution of 0.21 g (0.5 mmol) of X in 40 ml of DME was refluxed for $1\frac{1}{2}$ h with 0.4 g (10 mmol) of sodium hydroxide. Evaporation of the solution under vacuum gave a colorless solid (0.19 g) which on warming with benzene left an insoluble white solid (0.025 g, m.p. > 400°), the IR spectrum of which showed bands characteristic of $SiCH_3$ grouping.

The benzene-soluble portion was concentrated to give 0.16 g (85%) of *cis, cis*-1,2,3,4-tetraphenylbutadiene (XVIII), m.p. and mixture m.p. 183-184° [5]. NMR spectrum (CCl_4): δ 6.22 (s, 2H) and 7.03 ppm (m, 20 H).

Reaction of 1,1-dimethyl-2,5-diphenyl-1,silacyclopentadiene (V) with concentrated hydrochloric acid

A solution of 0.13 g (0.5 mmol) of V in 50 ml of DME was refluxed in the presence of 5 ml of concentrated hydrochloric acid for 2 h. The reaction mixture was neutralized and extracted with benzene. Removal of the solvent gave 0.08 g (80%) of *trans,trans*-1,4-diphenylbutadiene (XVII), m.p. and mixture m.p. 152-153° [11]. The benzene-insoluble portion (0.02 g, 15%, m.p. > 400°) gave IR bands characteristic of $SiCH_3$ grouping.

Reaction of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (X) with concentrated hydrochloric acid

A solution of 0.11 g (0.25 mmol) of X in 35 ml of DME was treated with 5 ml of concentrated hydrochloric acid. Immediately the solution became colorless and hot. On usual work-up of the solution 0.08 g (85%) of *cis,cis*-1,2,3,4-tetraphenylbutadiene (XVIII), m.p. 183-184° [5], was obtained together with 0.015 g (12%) of a polymeric material (m.p. > 400°) showing IR bands due to $SiCH_3$.

Reaction of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (X) with potassium

A solution of 0.42 g (1 mmol) of X in DME was flushed with pure and dry nitrogen and was shaken vigorously with 0.25 g (0.63 mmol) of freshly cut potassium with a few pieces of broken glass in a Schlenk funnel for 8 h. The solution which was initially blue in color and which turned red was drained into 75 ml of moist tetrahydrofuran. The solution was extracted with benzene and water repeatedly and the benzene extract was concentrated under vacuum. The residue was chromatographed over a neutral alumina column and the evaporation of the solvent from the petroleum-ether (b.p. 60-80°) fraction gave 0.19 g (65%) of α,α'-dibenzylstilbene (XIX), m.p. 184-185° (lit. [6] m.p. 184-185°). Anal. found: C, 93.48; H, 6.27. $C_{28}H_{24}$ calcd.: C, 93.33; H, 6.67%: IR spectrum: ν_{max}(KBr): 3100, 2980, 1600, 1490 s, 1450, 1440, 1175, 1070 s, 1025, 997, 962, 940, 905, 827, 768 s, 743 s and 698 cm^{-1}. UV spectrum: λ_{max}(CH_3OH): 262 (sh) (ϵ 3100), 259 (sh) (3600) and 241 (sh) (6700) nm. NMR spectrum (CCl_4): δ 3.46 (s, 4H, methylene protons) and 7.00 ppm (m, 20H, phenyl protons).

On evaporation of the methanol fraction, a polymeric material was obtained (0.05 g, 12%, m.p. > 400°) the IR spectrum of which showed bands characteristic of $SiCH_3$ grouping.

In a similar experiment, 0.54 g (1 mmol) of hexaphenylsilacyclopentadiene (XI) was shaken with 0.3 g (0.75 mmol) of freshly cut potassium metal in DME and the resultant red colored dianion was dumped in moist tetrahydrofuran. On usual work-up, 0.25 g (70%) of α,α'-dibenzylstilbene (XIX), m.p. 184-185° (lit. [6] m.p. 184-185°) and a polymeric material (0.13 g, 24%, m.p. > 400°) showing bands characteristic of $SiCH_3$ grouping in the IR spectrum (KBr) were obtained.

In yet another experiment, 0.48 g (1 mmol) of 1-methyl-1,2,3,4,5-pentaphenyl-1-silacyclopentadiene (XX) was vigorously shaken with 0.25 g (0.625 mmol) of freshly cut potassium metal in DME and then the red solution drained into moist tetrahydrofuran. On usual work-up of the reaction mixture, 0.21 g

(70%) of α,α'-dibenzylstilbene (XIX) [6], m.p. 184-185° was obtained. Also, 0.11 g (23%, m.p. > 400°) of a polymeric material showing characteristic $SiCH_3$ bands in the IR spectrum (KBr) was obtained.

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