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NICKEL-CATALYZED REACTION OF SILACYCLOPROPENES WITH ACETYLENES. A CONVENIENT ROUTE TO 1-SILACYCLOPENTA-2,4-DIENES

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Summary

The reaction of 1-silacyclopropenes prepared photochemically from phenylethynyldisilanes with acetylenes in the presence of a nickel catalyst has been investigated. The reaction of 1,1-dimethyl-2-phenyl-3-trimethylsilyl-, 1,1-dimethyl-2-phenyl-3-phenyldimethylsilyl-, 1-methyl-1,2-diphenyl-3-trimethylsilyl-, 1,1,2-triphenyl-3-trimethylsilyl- and 1-methyl-1-mesityl-2-phenyl-3-trimethylsilyl-1-silacyclopropene with a phenylsilylacetylene in the presence of $NiCl_2(PEt_3)_2$ afforded the respective 2,5-bis(silyl)-3,4-diphenyl-1-silacyclopenta-2,4-dienes in high yields. 1-Methyl-1,3-bis(trimethylsilyl)-2-phenyl-1-silacyclopropene reacted with phenyl(trimethylsilyl)acetylene to give 1-methyl-1,2,5-tris(trimethylsilyl)-3,4-diphenyl-1-silacyclopenta-2,4-diene and isomers, while 1,1-dimesityl-2-phenyl-3-trimethylsilyl-1-silacyclopropene afforded no 1-silacyclopenta-2,4-diene.

Introduction

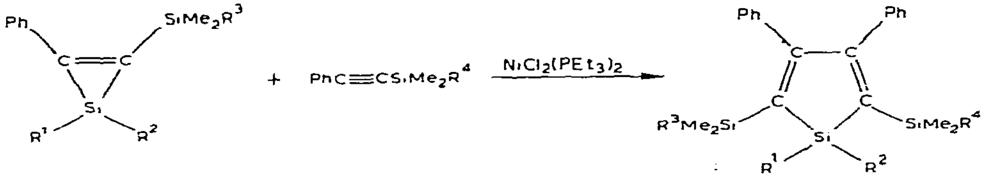
The chemistry of 1-silacyclopenta-2,4-dienes has attracted considerable interest over the past decade [1—7]. However, the synthetic route to these compounds are rather limited [8—13]. One of these involves the reaction of 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silacyclopropene with terminal and internal acetylenes, in some cases in the presence of a palladium catalyst [12]. The other comprises the reaction of 1,2-dihydrodisilanes with disubstituted acetylenes in the presence of dichlorobis(triethylphosphine)nickel(II) [13]. This reaction might possibly involve a transient nickelasilacyclobutene intermediate produced from a silylenoid species [14] and an acetylene. The nickelasilacyclobutene intermediate also might be expected to be formed by insertion of the nickel complex into a silacyclopropene. The intermediate thus produced then would react with an acetylene to give the silacyclopenta-2,4-diene.

In order to develop a convenient preparative route to silacyclopenta-2,4-dienes, we have investigated the reaction of the silacyclopropenes with acetylenes in the presence of a nickel catalyst.

Results and discussion

Recently we found that photolysis of phenylethynyldisilanes affords a convenient route to silacyclopropenes [15]. We have now carried out the reaction of these compounds with silyl-substituted phenylacetylenes in the presence of a nickel catalyst. The reaction of 1,1-dimethyl-2-phenyl-3-trimethylsilyl-1-silacyclopropene (I) with a small excess of phenyl(trimethylsilyl)acetylene in the presence of a catalytic amount of dichlorobis(triethylphosphine)nickel(II) at 135°C for 18 h in a sealed glass tube afforded 1,1-dimethyl-2,5-bis(trimethylsilyl)-3,4-diphenyl-1-silacyclopenta-2,4-diene (II) in 94% yield (Scheme 1). No other isomers could be detected either by spectroscopic or GLC analysis. A similar reaction of 1,1-dimethyl-2-phenyl-3-phenyldimethylsilyl-1-silacyclopropene (III) with phenyl(phenyldimethylsilyl)acetylene in the presence of the nickel catalyst gave 1,1-dimethyl-2,5-bis(phenyldimethylsilyl)-3,4-diphenyl-1-silacyclopenta-2,4-diene (IV) in 80% yield. All spectral data of IV were identical with those of a compound prepared from the reaction of 1,2-dihydrotetramethyldisilane with phenyl(phenyldimethylsilyl)acetylene in the presence of the same catalyst at 120°C. The location of the phenyldimethylsilyl groups on the five-membered ring in compound IV was confirmed by means of protodesilylation. Thus treatment of IV with dry hydrogen chloride in diethyl ether for 7 h at room temperature gave 2,3-diphenyl-1,3-butadiene in 84% yield. The production of 2,3-diphenyl-1,3-butadiene clearly indicates that the two silyl groups are located at 2- and 5-positions in the silacyclopenta-2,4-diene ring.

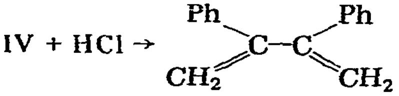
SCHEME 1



(I, R^1 = R^2 = R^3 = Me;
III, R^1 = R^2 = Me, R^3 = Ph;
VI, R^1 = R^3 = Me, R^2 = Ph;
VIII, R^1 = R^2 = Ph, R^3 = Me;
X, R^1 = R^3 = Me, R^2 = mesityl)

(II, R^1 = R^2 = R^3 = R^4 = Me;
IV, R^1 = R^2 = Me, R^3 = R^4 = Ph;
V, R^1 = R^2 = R^3 = Me, R^4 = Et;
VII, R^1 = R^3 = R^4 = Me, R^2 = Ph;
IX, R^1 = R^2 = Ph, R^3 = R^4 = Me;
XI, R^1 = R^3 = R^4 = Me, R^2 = mesityl)

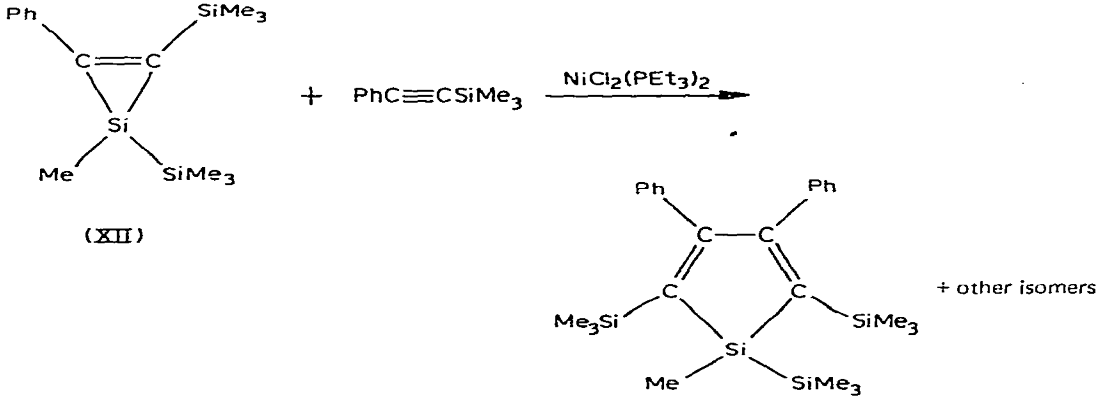
$$HMe_2SiSiMe_2H + PhC{\equiv}CSiMe_2Ph \xrightarrow{NiCl_2(PEt_3)_2} IV$$


$$IV + HCl \rightarrow CH_2{=}C(Ph){-}C(Ph){=}CH_2$$

The present method provides a convenient route to the unsymmetrical silyl-substituted 1-silacyclopenta-2,4-dienes which are accessible only with difficulty. Thus, the reaction of I with phenyl(ethyldimethylsilyl)acetylene under the same conditions produced 1,1-dimethyl-2-ethyldimethylsilyl-3,4-diphenyl-5-trimethylsilyl-1-silacyclopenta-2,4-diene (V) in 86% yield. Again, no other isomers were observed by spectroscopic analysis. Furthermore, this method is not restricted to production of the 1,1-dimethyl-1-silacyclopenta-2,4-dienes. 1-Methyl-1,2-diphenyl-3-trimethylsilyl-1-silacyclopropene (VI) reacted with phenyl(trimethylsilyl)acetylene in the presence of the nickel catalyst to give 1-methyl-1,3,4-triphenyl-2,5-bis(trimethylsilyl)-1-silacyclopenta-2,4-diene (VII) in 73% yield, and 1,1,2-triphenyl-3-trimethylsilyl-1-silacyclopropene (VIII) reacted with phenyl(trimethylsilyl)acetylene to give 1,1,3,4-tetraphenyl-2,5-bis(trimethylsilyl)-1-silacyclopenta-2,4-diene (IX) in 99% yield. The ^{1}H NMR, mass and IR spectra of compounds VII and IX were identical with those of authentic samples obtained from the reaction of 1,2-dimethyl-1,2-diphenyldisilane and 1,2-dihydrotetraphenyldisilane with phenyl(trimethylsilyl)acetylene in the presence of the nickel catalyst. Protodesilylation of IX by hydrogen chloride in benzene afforded 2,3-diphenylbutadiene in 40% yield, indicating that the two trimethylsilyl groups are attached to the carbon atoms at 2- and 5-positions inthe silacyclopenta-2,4-diene ring.

1-Methyl-1-mesityl-2-phenyl-3-trimethylsilyl-1-silacyclopropene (X) [16] also reacted with phenyl(trimethylsilyl)acetylene in the presence of the nickel catalyst and after 19 h afforded 1-silacyclopenta-2,4-diene (XI) in 86% yield. In this reaction, 8% of the starting X was recovered unchanged.

In contrast to the reaction shown in Scheme 1, 1-methyl-1,3-bis(trimethylsilyl)-2-phenyl-1-silacyclopropene (XII) * [17] reacted with phenyl(trimethylsilyl)acetylene in the presence of the nickel catalyst under the same conditions to give a mixture consisting of at least three products. A major product (42% yield) could be separated by GLC and identified as 1-methyl-1,2,5-tris(trimethylsilyl)-3,4-diphenyl-1-silacyclopenta-2,4-diene (XIII) by ^{1}H NMR, IR and



(XII)

(XIII)

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* This compound was air sensitive and had to be handled under an inert atmosphere.

TABLE 1

REACTION CONDITIONS AND YIELDS FOR 1-SILACYCLOPENTA-2,4-DIENES

Silacyclopropene (mg (mmol))	Acetylene (mg (mmol))	$NiCl_2(PEt_3)_2$ (mmol $\times 10^{-2}$)	Time (h)	Silacyclopentadiene and yield (%)	
I 154.1 (0.66)	171.0 [a] (0.98)	1.1	18	II	(94)
III 119.1 (0.40)	218.5 [b] (0.92)	0.9	18	IV	(80)
I 123.2 (0.53)	433.4 [c] (2.30)	0.7	16	V	(86)
VI 120.1 (0.41)	188.3 [a] (1.08)	1.0	15	VII	(73)
VIII 118.0 (0.33)	187.4 [a] (1.08)	1.1	15	IX	(99)
X 130.4 (0.39)	138.2 [a] (0.79)	1.2	19	XI	(86)
XII 173.6 (0.60)	139.6 [a] (0.80)	1.2	11	XIII	(42)

[a] $PhC{\equiv}CSiMe_3$. [b] $PhC{\equiv}CSiMe_2Ph$. [c] $PhC{\equiv}CSiMe_2Et$.

TABLE 2

MELTING POINTS, ELEMENTAL ANALYSIS, MASS AND IR DATA FOR 1-SILACYCLOPENTA-2,4-DIENES

Compound	m.p. (°C)	Found (calcd.) (%)		M^+	IR (cm^{-1})
		C	H		
II	96—97	70.72(70.86)	8.44(8.42)	406	1510, 1550
IV	— [a]	76.51(76.92)	7.27(7.21)	530	1505, 1545
V	95—96	71.16(71.36)	8.81(8.62)	420	1510, 1545
VII	150	74.56(74.29)	7.88(7.74)	468	1515, 1550
IX	209—210	76.83(76.92)	7.57(7.21)	530	1510, 1545
XI	128—130	75.27(75.22)	8.49(8.29)	510	1505, 1545
XIII	62	67.48(67.17)	8.80(8.67)	464	1530

[a] Liquid.

TABLE 3

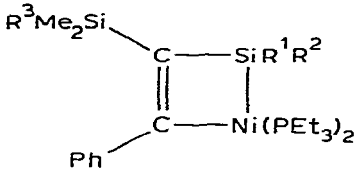
PROTON NMR CHEMICAL SHIFTS FOR 1-SILACYCLOPENTA-2,4-DIENES

Compound	Chemical shifts (δ, ppm) in CCl_4
II	—0.16 (Me_3Si, s, 18H), 0.41 (Me_2Si, s, 6H), 6.6—7.2 (ring protons, m, 10H)
IV	0.02 (Me_2Si, s, 12H), 0.06 (Me_2Si, s, 6H), 6.6—7.4 (ring protons, m, 20H)
V	—0.20 (Me_2Si, s, 6H), —0.18 (Me_3Si, s, 9H), 0.25 (CH_2Si, m, 2H), 0.39 (Me_2Si, s, 6H), 0.80 (CH_3C, m, 3H), 6.7—7.1 (ring protons, m, 10H)
VII	—0.34 (Me_3Si, s, 18H), 0.76 (MeSi, s, 3H), 6.8—7.6 (ring protons, m, 15H)
IX	—0.42 (Me_3Si, s, 18H), 6.8—7.9 (ring protons, m, 20H)
XI	—0.33 (Me_3Si, s, 18H), 0.72 (MeSi, s, 3H), 2.29 (CH_3C, broad s, 3H), 2.43 (CH_3C, broad s, 3H), 2.56 (CH_3C, broad s, 3H), 6.7—7.2 (phenyl and mesityl ring protons, m, 12H)
XIII	—0.14 (Me_3Si, s, 18H), 0.22 (Me_3Si, s, 9H), 0.52 (MeSi, s, 3H), 6.7—7.3 (ring protons, m, 10H)

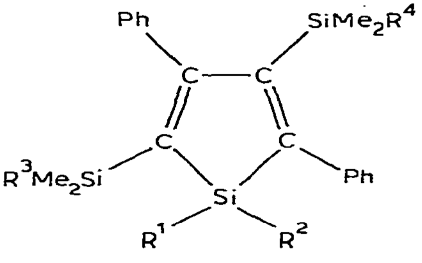
mass spectrometric analysis. Unfortunately, other products could not be separated by either GLC or HLPC. However, the molecular weight of the mixture, determined by mass spectrometric analysis, was consistent with the calculated value for $C_{26}H_{40}Si_4$.

The reaction conditions and yields of 1-silacyclopenta-2,4-dienes are summarized in Table 1. Melting points and analytical data, and ^1H NMR data for all 1-silacyclopenta-2,4-dienes reported here are listed in Tables 2 and 3.

Although the mechanism for the formation of 1-silacyclopenta-2,4-dienes is not clear, a nickelasilacyclobutene (A) might be involved as a key intermediate in the present reaction. The 1-silacyclopenta-2,4-diene would be produced from the reaction of this intermediate with a phenyl(silyl)acetylene. If this is true, the structure of the 1-silacyclopenta-2,4-dienes may depend highly on the steric interactions between intermediate A and an acetylene in the transition state.



(A)

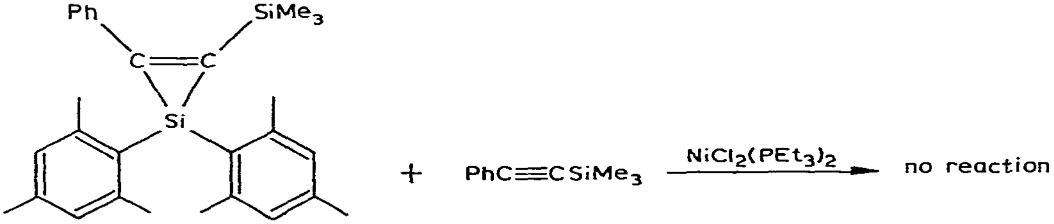


(B)

The formation of 2,5-bis(silyl)-3,4-diphenyl-1-silacyclopenta-2,4-dienes is apparently sterically favored over that of the isomer, 2,4-bis(silyl)-3,5-diphenyl-1-silacyclopenta-2,4-diene (B).

The formation of the metallasilacyclobutene intermediate has also been proposed in the reaction of 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silacyclopropene [12] or compound I [10] with an acetylene in the presence of a palladium catalyst.

A kinetically stable silacyclopropene, 1,1-dimesityl-2-phenyl-3-trimethylsilyl-1-silacyclopropene (XIV) [16], however, did not react with acetylenes under the same conditions as above. Thus, heating XIV with phenyl(trimethylsilyl)acetylene in the presence of the nickel catalyst at 135°C for 27 h led to complete recovery of the starting silacyclopropene XIV. The bulky mesityl groups presumably prevent the formation of a nickelasilacyclobutene analogous to A.



(XIV)

Experimental

General procedure

Proton NMR spectra were determined at ambient temperature with a JEOL Model JNM-MH-100 spectrometer using carbon tetrachloride solutions (containing cyclohexane (δ 1.44 ppm) as internal standard. Mass spectra were obtained on a JEOL Model JMS-D 300 equipped with a JMA-2000 data processing system. The ionizing voltage was 24 eV for all compounds.

Materials

Silacyclopropenes, I [15a,15b], III [15c], VI [15c], VIII [15c], X [16] and XIV [16], were prepared as reported in the literature.

Preparation of 2-phenylethynylheptamethyltrisilane

In a 100-ml flask was placed a solution of 2.5 g (24.5 mmol) of phenylacetylene in 10 ml of dry hexane. To this was added 11.5 ml of a butyllithium-hexane solution (1.6 *M*) at —78°C for 10 min. The mixture was stirred for 30 min at room temperature and then 3.9 g (17.4 mmol) of 2-chloroheptamethyltrisilane [18] in 20 ml of hexane was added to the mixture at room temperature. After refluxing for 2 h, the reaction mixture was hydrolyzed with water. The organic layer was separated and washed with water, and then dried over potassium carbonate. After evaporation of the solvent, the residue was distilled under reduced pressure to give 3.3 g (65% yield) of a colorless liquid, b.p. 102°C/2 Torr, n_D^{20} 1.5369; IR 2155 cm^{-1}; ^{1}H NMR δ (ppm) 0.21 (Me$_3$Si, s, 18 H), 0.27 (MeSi, s, 3 H), 7.1—7.5 (ring protons, m, 5 H) (Found: C, 62.29; H, 9.12, $C_{15}H_{26}Si_3$ calcd.: C, 61.99; H, 9.02%).

Preparation of 1-methyl-1,3-bis(trimethylsilyl)-2-phenyl-1-silacyclopropene (XII)

A solution of 5.15 g (17.7 mmol) of 2-phenylethynylheptamethyltrisilane dissolved in 500 ml of dry hexane was placed in a 500-ml pyrex reaction vessel, fitted with a 15 W low-pressure immersion mercury lamp having a Vycor filter. The mixture was irradiated at room temperature with a slow stream of nitrogen bubbling through the mixture. After 5.5 h of irradiation, almost 100% of the starting 2-phenylethynylheptamethyltrisilane was photolyzed. Most of the solvent was evaporated under a nitrogen atmosphere and the residue that remained was distilled under reduced pressure through a short column to give 1.5 g (29% yield) of silacyclopropene XII. ^{1}H NMR δ (ppm) in C_6D_6 0.18 (Me$_3$Si, s, 9 H), 0.25 (MeSi, s, 3 H), 0.38 (Me$_3$Si, s, 9 H), 6.9—7.8 (ring protons, m); exact mass, found: 290.1333. $C_{15}H_{26}Si_3$ calcd.: 290.1342.

Preparation of 1-silacyclopenta-2,4-dienes

The following is typical of the procedures used. A mixture of 0.1736 g (0.60 mmol) of XII, 0.0408 g (0.21 mmol) of tetradecane as an internal standard, 0.1396 g (0.80 mmol) of phenyl(trimethylsilyl)acetylene and 4.4 mg (1.2 × 10^{-2} mmol) of dichlorobis(triethylphosphine)nickel(II) was placed in a carefully dried 4-ml glass tube, previously flushed with argon. The glass tube was sealed under reduced pressure and then heated for 11 h at 135°C. GLC analysis of the reaction mixture showed the presence of XIII (42% yield) and isomers of XIII

(36% yield, M^+ 464). Pure XIII was isolated by preparative GLC. Silacyclopenta-2,4-dienes, II, IV, V, XI and XIII, were isolated by preparative GLC, and VII and IX were obtained by recrystallization of the reaction mixture from ethanol. The reaction conditions and yields of the products obtained are listed in Table 1.

Reaction of 1,2-dihydrodisilanes with phenylsilylacetylene in the presence of $NiCl_2(PEt_3)_2$

A mixture of 0.3733 g (3.15 mmol) of 1,2-dihydrotetramethyldisilane, 1.3216 g (5.59 mmol) of phenyl(phenyldimethylsilyl)acetylene and 4.8 mg (1.3×10^{-2} mmol) of $NiCl_2(PEt_3)_2$ was heated at 120°C for 15 h in a sealed glass tube. GLC analysis of the mixture indicated the presence of IV (33% yield). The mixture was distilled under reduced pressure to give volatile products. Pure IV was isolated by preparative GLC. Similarly, VII (from 1,2-dimethyl-1,2-diphenyldisilane, 0.4656 g (1.92 mmol), phenyl(trimethylsilyl)acetylene, 0.6358 g (3.65 mmol) and $NiCl_2(PEt_3)_2$, 5.0 mg (1.4×10^{-2} mmol)) and IX (from 1,2-dihydrotetraphenyldisilane, 0.7458 g (2.03 mmol), phenyl(trimethylsilyl)acetylene, 0.8469 g (4.86 mmol) and $NiCl_2(PEt_3)_2$, 7.1 mg (1.9×10^{-2} mmol)) were obtained in 40 and 60% yield, respectively.

Protodesilylation of IV

In a 50-ml two-necked flask fitted with a condenser and an inlet tube for hydrogen chloride was placed a solution of 0.2876 g (0.54 mmol) of IV in 25 ml of diethyl ether. Hydrogen chloride gas was passed into the solution for 7 h at room temperature. The mixture was washed with water to neutral and dried over potassium carbonate. GLC analysis of the mixture showed the production of 2,3-diphenyl-1,3-butadiene (84% yield). The pure compound was isolated by GLC, m.p. 46°C (lit. 47—48°C [19]), mass spectrum *m/e* 206; ^1H NMR δ (ppm) 5.20 and 5.42 ($^1H^2HC=C$, d, $J = 1.5$ Hz, 4 H), 7.0—7.4 (ring protons, m, 10 H).

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