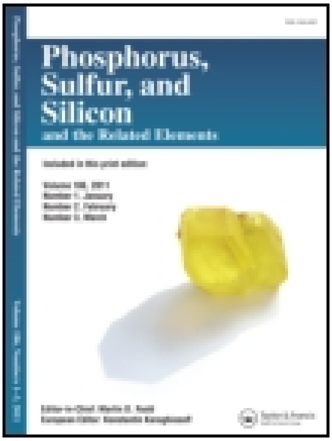

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Multicomponent Reactions (MCRs) Leading to Silaheterocycles via Dianion Cyclization

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To cite this article: M. S. Singh & Pratibha Singh (2007) Multicomponent Reactions (MCRs) Leading to Silaheterocycles via Dianion Cyclization, Phosphorus, Sulfur, and Silicon and the Related Elements, 182:4, 835-843, DOI: 10.1080/10426500601061991

To link to this article: http://dx.doi.org/10.1080/10426500601061991

Phosphorus, Sulfur, and Silicon, 182:835–843, 2007

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500601061991

Multicomponent Reactions (MCRs) Leading to Silaheterocycles via Dianion Cyclization

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Nucleophilic asymmetrical Schiff base that incorporating aromatic rings to induce rigidity to the system was prepared by the condensation of o-*hydroxyacetophenone and salicylaldehyde hydrazone in a 1:1 molar ratio. A useful sequence of reactions for the synthesis of a variety of previously unknown silaheterocycles is described. The reaction of salicylidene* o-*hydroxyacetophenone with sodium hydride in dioxane produces a 1,10-remote dianion. The cyclization of this dianion with diorganodichlorosilanes affords dibenzodioxadiazasilaundecines in good yields. The products were characterized by satisfactory elemental analyses and spectral (IR, ^{1}H, ^{13}C, ^{29}Si NMR, and mass) studies.*

Keywords dianion; dibenzodioxadiazasilaundecines; diorganodichlorosilanes; electrophilic cyclizations; *o*-hydroxyacetophenone; salicylaldehyde hydrazone

INTRODUCTION

Schiff bases have been used as precursors and intermediates for the synthesis of a variety of organic compounds useful in analytical, medicinal, polymer, and liquid crystalline materials[1] or as ligands for complexation. Monocyclic medium-ring heterocycles are an extremely important class of compounds, which occur in a range of natural and unnatural products. Cyclocondensation reactions are recognized as worthwhile synthetic methods for preparing heterocyclic compounds.[2] Increasing interest has been paid for several years to the chemistry of heterocycles containing tin and silicon due to their unique properties and remarkable potential biological activity.[3,4] Monocyclic eight-membered silicon-containing[5] heterocycles have been prepared by condensation

Received June 26, 2006; accepted September 11, 2006.

The authors are grateful for financial support of this work from the Council of Scientific and Industrial Research (CSIR), New Delhi, India.

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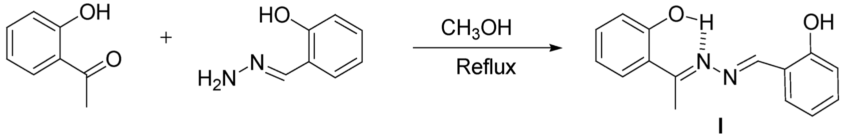
reactions.[6] Chlorosilanes are synthetic intermediates in the preparation of all classes of organosilicon compounds.[7,8] A variety of silaheterocycles have been obtained by intramolecular carbene or carbenoid pathways from silyldiazoacetic esters.[9] Organosilicon complexes with O and N donor ligands have been reported[10,11]and are widely used in medicinal and pharmaceutical chemistry.[12] Certain organosilicon compounds have been extensively used in chemical vapor deposition and deoxygenation reactions in organic transformations.[13] Strategies involving dianion reactions[14–16] have become powerful and versatile tools in organic synthesis and have developed as a powerful method for preparing various types of carbocyclic and heterocyclic compounds via carbon-carbon and carbon-heteroatom bond-forming processes. To the best of our knowledge, there are no reports on the synthesis of eleven-membered silaheterocycles containing five heteroatoms (N, O, and Si). Our aim is to broaden the range of useful silaheterocycles, which may provide an easy access to synthetic intermediates and therapeutic agents. With this background, the goal of the present article is to provide cyclization reactions of remote dianion via cyclosilylation. A remarkable feature of this reaction is the construction of oxygen-silicon bonds via a tandem process. In our continuing studies on the synthesis of new heterocyclic systems[17–20] using efficient intermolecular cyclization reactions via a dianion intermediate, we herein describe the preparation of novel, previously unknown dibenzodioxadiazasilaundecines in good yields.

RESULTS AND DISCUSSION

The reaction of equimolar amounts of salicylaldehyde hydrazone and *o*-hydroxyacetophenone in methanol under reflux for 2 h according to the literature method[21,22] afforded the corresponding salicylidene-*o*-hydroxyacetophenone (**I**) (Scheme 1). The structure of ligand (**I**) was established from its spectral and analytical data. The IR spectrum showed peaks at 3435 cm^{-1} for the hydroxyl group and at 1633 and 1689 cm^{-1} for C=N groups. In its ^{1}H NMR spectrum two singlets at δ 13.13 and δ 11.05 ppm exhibited for two unsymmetrical OH groups

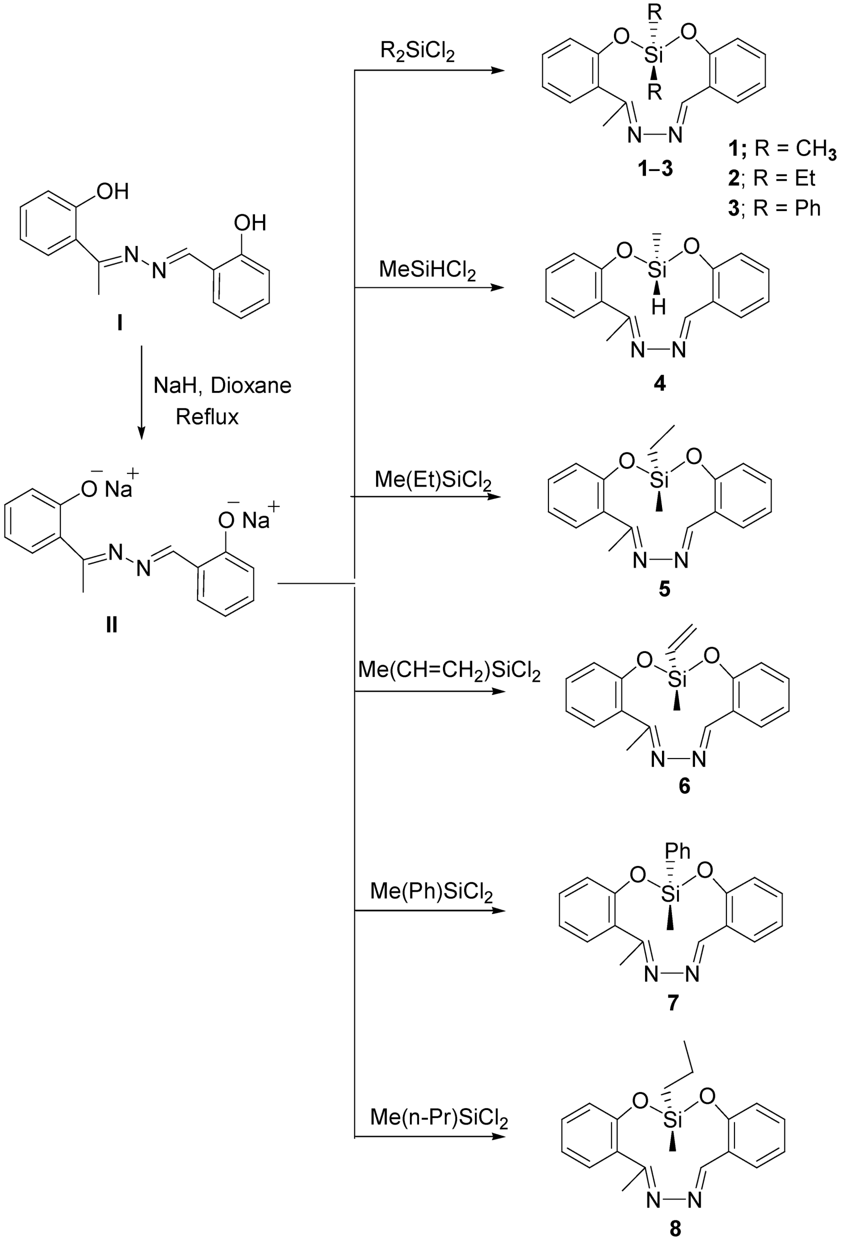


SCHEME 1

that are D_2O exchangeable, and the downfield signal of –OH group suggests that there is intramolecular hydrogen bonding between this OH and one of the azomethine nitrogen. The azomethine proton of the CH=N group manifested at δ 8.94 ppm as a sharp singlet. A multiplet in the range δ 7.00–7.91 for aromatic protons and a sharp singlet at δ 2.73 for methyl protons attached to C=N has been observed.

The introduction of the diorganosilylene group is normally achieved by the reaction of diorganodichlorosilane with a proper substrate in the presence of a base to prepare heterocyclic compounds containing a silicon atom. Our synthesis involves the initial formation of dianion **II** from sequential deprotonations of the phenolic OH groups of ligand (**I**) by sodium hydride in dry dioxane. The 1,10-dianion thus generated attacks to a variety of diorganodichlorosilanes leading to the formation of compounds **1**–**8** (Scheme 2). The beauty of the reaction procedure resides in in situ formation of remote dianion and further cyclization so that the multistep reaction sequence is synchronized in a simple one pot. TLC of all compounds confirmed their purity. The compounds dibenzodioxadiazasilaundecines are characterized on the basis of satisfactory elemental analyses (Table I) and spectral (IR, ^{1}H, ^{13}C, ^{29}Si NMR, and mass) studies (Table II).

The disappearance of absorption band and signals corresponding to –OH group in both IR and ^{1}H NMR spectra and the appearance of a new band in the region 1048–1023 cm^{-1} may be assigned to a Si-O bond,[23] suggesting the cyclic structure of prepared compounds. The IR spectra exhibited C=N absorptions in the range 1600–1625 cm^{-1} and Si-C absorptions in the range 1265–1275 cm^{-1}. The lowering of ν(C=N)[24] by 33–55 cm^{-1} is a further indication of the coordination of C=N to the silicon atom exhibiting hexa-coordinated state, which is further supported by ^{29}Si NMR chemical shifts. ^{1}H NMR spectra displayed a singlet at δ 8.71 ppm for the azomethine proton, a multiplet in the range δ 6.83–7.74 for aromatic protons, a singlet around δ 2.62 for the methyl proton, and singlets of silicon methyl in the range δ 0.11–0.70. The signals for the vinyl and n-propyl protons were visible in the expected regions. The alkyl groups attached to silicon displayed single resonance for chemically equivalent protons and carbons. In addition, ^{13}C NMR spectra supported the assigned structures. The extremely high-field shifts of the ^{29}Si NMR signals of the compounds indicate the presence of hexacoordinate[25] silicon in all the compounds. Since the R group is bound directly to the ^{29}Si nucleus, it is not surprising that the value of δ depends primarily on the nature of this R group. When R = phenyl, the chemical shift is consistently more negative (by about 25 ppm) than R = alkyl. Although the alkyl moiety has a greater electron pushing capacity (σ donation) than the aryl, the delocalized π system in the


OH
OH
N
N
I
NaH, Dioxane
Reflux
O⁻ Na⁺
O⁻ Na⁺
II
R₂SiCl₂
1–3
1; R = CH₃
2; R = Et
3; R = Ph
MeSiHCl₂
4
Me(Et)SiCl₂
5
Me(CH=CH₂)SiCl₂
6
Me(Ph)SiCl₂
7
Me(n-Pr)SiCl₂
8
O
Si
H
Ph
N

SCHEME 2

TABLE I Synthetic and Analytical Data of Compounds 1–8

Compound/Mol. Wt.	Reactants, mg (mmole)						Analysis: % Found (Calcd.)		
Calcd. (Found)	L	NaH	R_2SiCl_2	Molar ratio	Yield (%)	M.P. (°C)	C	H	N
(**1**) $C_{17}H_{18}N_2O_2Si$ 310 (310.41)	508 (2.0)	96 (4.0)	258 (2.0)	1:2:1	72	165	65.43 (65.78)	5.46 (5.85)	9.31 (9.02)
(**2**) $C_{19}H_{22}N_2O_2Si$ 338 (338.46)	508 (2.0)	96 (4.0)	314 (2.0)	1:2:1	70	195	67.64 (67.42)	6.23 (6.55)	8.14 (8.28)
(**3**) $C_{27}H_{22}N_2O_2Si$ 434 (434.55)	508 (2.0)	96 (4.0)	506 (2.0)	1:2:1	71	155	74.39 (74.63)	5.37 (5.10)	6.12 (6.45)
(**4**) $C_{16}H_{16}N_2O_2Si$ 296 (296.38)	508 (2.0)	96 (4.0)	230 (2.0)	1:2:1	67	210	64.56 (64.84)	5.27 (5.44)	9.13 (9.45)
(**5**) $C_{18}H_{20}N_2O_2Si$ 324 (324.43)	508 (2.0)	96 (4.0)	286 (2.0)	1:2:1	62	155	66.17 (66.63)	6.01 (6.21)	8.22 (8.63)
(**6**) $C_{18}H_{18}N_2O_2Si$ 322 (322.42)	508 (2.0)	96 (4.0)	282 (2.0)	1:2:1	64	207	67.16 (67.05)	5.31 (5.62)	8.39 (8.68)
(**7**) $C_{22}H_{20}N_2O_2Si$ 372 (372.48)	508 (2.0)	96 (4.0)	382 (2.0)	1:2:1	66	163	70.58 (70.93)	5.82 (5.41)	7.35 (7.52)
(**8**) $C_{19}H_{22}N_2O_2Si$ 338 (338.46)	508 (2.0)	96 (4.0)	314 (2.0)	1:2:1	68	212	67.14 (67.42)	6.23 (6.55)	8.03 (8.29)

TABLE II Spectral Data of Compounds 1–8

Compound no.	IR (KBr, cm^{-1})	NMR		
		^{1}H	^{13}C	^{29}Si
1	1612, 1273, 964, 565	8.71 (s, 1H, CH=N), 6.90–7.74 (m, 8H, ArH), 2.62 (s, 3H, CH$_3$), 0.11 (s, 6H, CH$_3$)	170.27, 164.62, 163.36, 160.42, 159.62, 133.25, 132.75, 132.66, 132.59, 119.54, 119.25, 118.15, 117.19, 117.07, 29.41, 10.12	−138.63
2	1620, 1271, 895, 535	8.71 (s, 1H, CH=N), 6.93–7.74 (m, 8H, ArH), 2.62 (s, 3H, CH$_3$), 0.98 (t, J = 4.0 Hz, 6H, CH$_3$), 0.58 (quartet, J = 2.0 Hz, 4H, CH$_2$)	170.17, 164.72, 163.16, 160.62, 159.82, 133.45, 132.95, 132.56, 132.49, 119.74, 119.00, 118.05, 117.29, 117.17, 29.71, 6.55, 1.02	−142.42
3	1620, 1271, 895, 522	8.71 (s, 1H, CH=N), 6.83–7.74 (m, 18H, ArH), 2.62 (s, 3H, CH$_3$)	170.14, 168.07, 164.68, 163.17, 159.73, 134.42, 133.42, 132.55, 130.19, 128.94, 127.76, 118.81, 117.13, 14.76	−162.27
4	1621, 1275, 980, 562	8.70 (s, 1H, CH=N), 6.93–7.65 (m, 8H, ArH), 2.60 (s, 3H, CH$_3$), 4.72 (s, 1H, Si-H), 0.11 (s, 3H, CH$_3$)	170.37, 164.42, 163.76, 160.22, 159.32, 133.85, 132.65, 132.86, 132.79, 119.56, 119.12, 118.17, 117.19, 29.21, 8.55	−140.58
5	1622, 1275, 894, 524	8.70 (s, 1H, CH=N), 6.93–7.74 (m, 8H, ArH), 2.58 (s, 3H, CH$_3$), 0.94 (t, J = 4.0 Hz, 3H, CH$_3$), 0.54 (quartet, J = 3.0 Hz, 2H, CH$_2$); 0.11 (s, 3H, CH$_3$)	164.17, 163.16, 159.82, 155.23, 132.94, 128.94, 119.74, 117.23, 42.68, 29.69, 14.78, 10.27	−146.07
6	1619, 1270, 967, 563	8.70 (s, 1H, CH=N), 6.93–7.64 (m, 8H, ArH), 5.97 (m, 3H, CH=CH$_2$), 2.59 (s, 3H, CH$_3$), 0.19 (s, 3H, CH$_3$)	170.15, 168.06, 164.70, 159.78, 136.18, 133.40, 132.56, 129.08, 119.72, 118.83, 117.28, 29.71, 10.46, 1.03, 0.57	−154.63
7	1612, 1269, 837, 520	8.71 (s, 1H, CH=N), 6.93–7.64 (m, 13H, ArH), 2.62 (s, 3H, CH$_3$), 0.40 (m, 3H, CH$_3$)	170.17, 164.72, 160.60, 133.42, 132.49, 129.08, 127.80, 119.74, 117.04, 11.86	−163.23
8	1614, 1269, 839, 549	8.71 (s, 1H, CH=N), 6.93–7.67 (m, 8H, ArH), 2.62 (s, 3H, CH$_3$), 1.40 (t, J = 4.0 Hz, 3H, CH$_3$), 1.01 (m, 2H, CH$_2$), 0.57 (t, J = 4.0 Hz, 2H, CH$_2$), 0.12 (s, 3H, CH$_3$)	170.31, 168.10, 162.72, 160.80, 159.57, 158.55, 136.27, 133.24, 132.66, 129.69, 119.60, 118.71, 117.28, 116.35, 27.62, 15.56, 14.57, 10.63	−147.63

phenyl-substituted compound allows for dπ-pπ interaction to dominate the overall shielding of the ^{29}Si nucleus.[26] Mass spectroscopic data of the compounds established their monomeric nature. The newly synthesized silaheterocyclic rings gained rigidity due to the presence of two benzene rings in their skeleton.

In conclusion, a simple work-up, low consumption of the solvent, fast reaction rates, a mild reaction condition, good yields, and selectivity of the reaction make this method a very appealing and useful contribution to the preparation of a rare class of silaheterocycles.

EXPERIMENTAL

Chemicals were obtained from Sigma-Aldrich (St. Louis, USA), Merck (Darmstadt, Germany), Fluka (Buchs, Switzerland), and Lancaster (Lancanshire, England), and are used as such without further purification. All solvents (Analytical Reagents (AR) or extra pure grade) used for spectroscopic and other physical studies were further purified by literature methods.[27] All operations were performed under a nitrogen atmosphere using standard glasswares. Infrared spectra were recorded as KBr discs on an FT-IR Perkin-Elmer model RX-I and on JASCO FT/IR-5300 spectrophoto-meters. Melting points were determined using a calibrated thermometer by Remi Digital Melting Point apparatus and are uncorrected. Elemental analyses were performed by Central Drug Research Institute, Lucknow. NMR (^{1}H, ^{13}C, and ^{29}Si) spectra were recorded on a JEOL AL 300 instrument (Japan). All chemical shifts were reported in parts per million relative to TMS as an internal standard in $CDCl_3$. Mass spectra were recorded at 70 eV ionizing voltage on a JEOL-D300 MS instrument.

Synthesis of Salicylidene-*o*-hydroxyacetophenone (I)

The Schiff base **I** was prepared by simple condensation of salicylaldehyde hydrazone (4.76 g, 35 mmoles) and *o*-hydroxyacetophenone (4.76 g, 35 mmoles) in dry methanol (150 mL). The reaction mixture was stirred at reflux for 2 h and cooled to r.t. The yellow needles of salicylidene-*o*-hydroxyacetophenone thus obtained were washed with methanol, dried, and recrystallized from ethanol.

I: Yield, 6.13 g, (70%), m.p. 159°C; IR (KBr, cm^{-1}): 3435, 1633, 1689; ^{1}H NMR (300 MHz, $CDCl_3$, δ): 13.13 (s, 1H, OH, D_2O exchangeable), 11.05 (s, 1H, OH, D_2O exchangeable), 8.94 (s, 1H, CH=N), 7.00–7.91 (m, 8H, ArH), 2.73 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 170.14, 168.05, 164.67, 160.60, 159.77, 133.41, 132.92, 132.55, 129.07, 119.74, 118.96, 118.02, 117.62, 117.4, 14.78. MS: m/z (M^+) 254.27; anal.

calcd. for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.43; H, 5.22; N, 10.81.

Synthesis of Dibenzodioxadiazasilaundecine [1]

To a stirred suspension of NaH (96 mg, 4 mmoles) in dry dioxane (5 mL) was added dioxane solution (55 mL) of ligand **I** (508 mg, 2 mmoles) dropwise with constant stirring and, it was refluxed for 4 h in an inert atmosphere. Thus the yellowish brown solution of dianion generated in situ was cooled to r.t. dichlorodimethylsilane (258 mg, 2 mmoles) was added dropwise with constant stirring, and the reaction mixture was refluxed for an additional 5 h. Completion of the reaction was checked by TLC. The reaction mixture was evaporated with the help of a rotary evaporator, and the residue obtained was subjected to solumn chromatography (n-hexane/ethyl acetate, 8:1) to give **1**. All other silaheterocycles (**2–8**) were also synthesized analogously as previously described in the desired molar ratios. The analytical and spectral data for compounds **1** to **8** are listed in Tables I and II, respectively.

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