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Siliranes: Formation, Isonitrile Insertions, and Thermal Rearrangements

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Abstract: The siliranes **7-10** and **22** as well as the vinylsiliranes **14-16**, **20**, and **21** are prepared by [1+2]-cycloadditions of silylene **2** with alkenes and dienes. The first isonitrile insertion products, the silacyclobutanimines **26-28** were synthesized and the structure of **28** was determined by X-ray crystallography. Upon thermolysis **20-22** rearranged quantitatively to furnish the compounds **29-32**.
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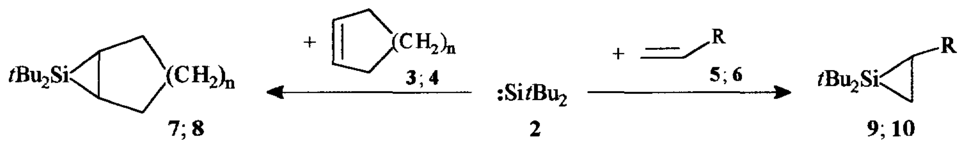
Although silylenes and siliranes bearing bulky substituents have been known for a considerable time, their synthetic potential has by no means been fully exploited. In particular, only very few routes are available for the preparation of alkyl-substituted representatives.[1] Previous work performed in our laboratory has established hexa-*tert*-butylcyclotrisilane **1** as an ideal starting material for the photochemical generation of di-*tert*-butylsilylene **2**.

$$\underset{\mathbf{1}}{(\mathrm{Si}t\mathrm{Bu}_2)_3} \xrightarrow[-\,t\mathrm{Bu}_2\mathrm{Si{=}Si}t\mathrm{Bu}_2]{h\nu} \underset{\mathbf{2}}{:\mathrm{Si}t\mathrm{Bu}_2}$$

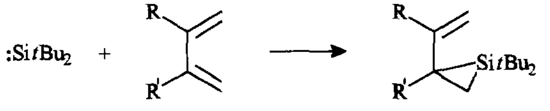
The chemistry of **2** has been investigated over the past ten years. Thus, for example, reactions of this species with nitriles, isonitriles, ketones, 1,4-dihetero-1,3-dienes, and other multiple bond systems have been realized.[1] However, the important groups of the alkenes and 1,3-dienes were missing from this series.

Upon photolysis of hexa-*tert*-butylcyclotrisilane in the presence of alkenes or open-chain and cyclic 1,3-dienes, the generated di-*tert*-butylsilylene participates in a [1+2]-cycloaddition to furnish siliranes (see Table 1). In the cases of cyclopentene **3**, cyclohexene **4**, and the monosubstituted ethylenes **5** and **6**, the respective siliranes **7-10** are obtained as air-sensitive, colourless oils in good to very good yields.



3; **7**: n = 1 **4**; **8**: n = 2 **5**; **9**: R = 2-MePh **6**; **10**: R = CH_2Ph

Siliranes **7** and **8** have previously been obtained by reduction of di-*tert*-butyldichlorosilane in the presence of the corresponding alkene.[2] Open-chain 1,3-dienes such as **11-13** react with the silylene to furnish the vinylsiliranes **14-16**. These products are also air-sensitive, colourless oils which, in the pure state, are only stable at room temperature for short times.



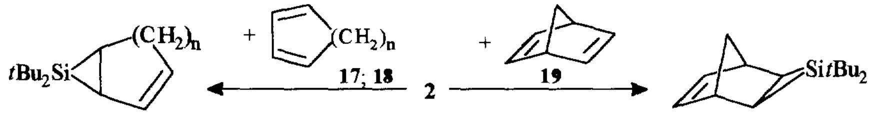
11-13 **14-16**

11; **14**: R = R' = Me
12; **15**: R = R' = OMe
13; **16**: R = Me, R' = H

The fact that the vinylsiliranes can be isolated is worthy of note since the previously reported reactions of practically all silylenes including those bearing very voluminous substituents had given rise to [1+4]-cycloaddition products exclusively. With dimesitylsilylene, generated by photolysis of 2,2-dimesitylhexamethyltrisilane, it was possible to characterize mixtures of [1+2]- and [1+4]-cycloadducts, but no pure vinylsilirane was isolated.[3]

The [1+2]-cycloadducts **20-22** are isolated in yields between 77 and 100% from the reactions of silylene **2** with carbocyclic 1,3-dienes **17** and **18** or with norbornadiene **19**.

17; **20**: n = 1
18; **21**: n = 2



20; **21** **22**

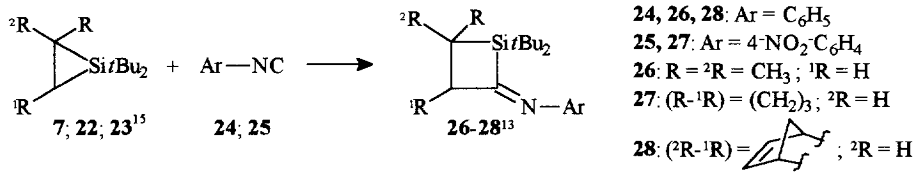
All siliranes were isolated by short path distillation and characterized by complete spectroscopic analysis (see Table 1 and ref. 4).

Table 1: ^{29}Si NMR data, yields, boiling and melting points of the siliranes.

#	silirane	^{29}Si-δ [ppm]	yield [%]	bp and mp
1	**7**	-39.51	86	~ 34 °C / 0.01 mbar
2	**8**[5]	-54.63	92	35-40 °C / 0.01 mbar; mp.: 26-28 °C
3	**9**[6]	-49.97	44	62-64 °C / 0.02 mbar
4	**10**	-49.04	>95	61-68 °C / 0.05 mbar
5	**14**[6]	-44.21	40	42-45 °C / 2.5 mbar
6	**16**[6]	-48.59	36	52 °C / 1.5 mbar
7	**15**	-44.91	37	35-45 °C / 0.05-0.1 mbar
8	**21**	-45.39	77	38-40 °C / 0.01 mbar; mp.: 12 °C
9	**20**[7]	-55.99	84	60-70 / 1-1.5 mbar
10	**22**	3.64	>95	75 °C / 0.8 mbar; mp.: 12-14 °C

A characteristic feature for siliranes is a ^{29}Si NMR signal in the high field region between -40 and -80 ppm.[8] Therefore it was surprising that the tricyclic compound **22** showed a resonance at 3.64 ppm. In order to prove the silirane structure of this substance, it was converted into a crystalline material. Insertion reactions of siliranes with olefins,[9] aldehydes and ketones,[10] silylenes,[11] and chalcogenes[12] are well known, but reactions with isocyanides are described here for the first time. Phenyl isonitrile **24** and *para*-nitrophenyl isonitrile **25** also underwent insertion into the Si-C bond at room temperature with formation of the silacyclobutanimines **26-**

28[13]. The structure of **28** has been elucidated by X-ray crystallography (see Fig. 1 and ref. 14). The molecule exhibits a practically planar silacyclobutane ring with stretched Si-C and C-C bonds. The phenyl group has a *cis* orientation to the Si*t*Bu$_2$ unit so that the Si-C-N angle is increased to 147°.



7; 22; 23[15] **24; 25** **26-28**[13]

24, 26, 28: Ar = C_6H_5
25, 27: Ar = 4-NO_2-C_6H_4
26: R = ^{2}R = CH_3 ; ^{1}R = H
27: (R-^{1}R) = $(CH_2)_3$; ^{2}R = H
28: (^{2}R-^{1}R) = ; ^{2}R = H

These results show that isonitrile insertions into Si-C bonds of siliranes provide an access to the novel silacyclobutanimine class of compounds.

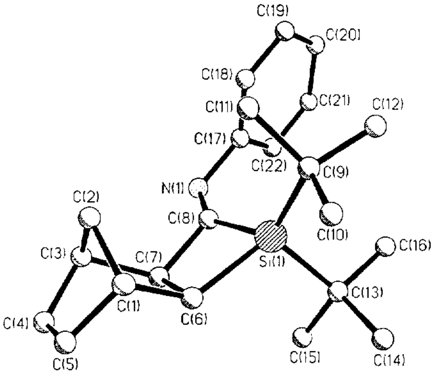
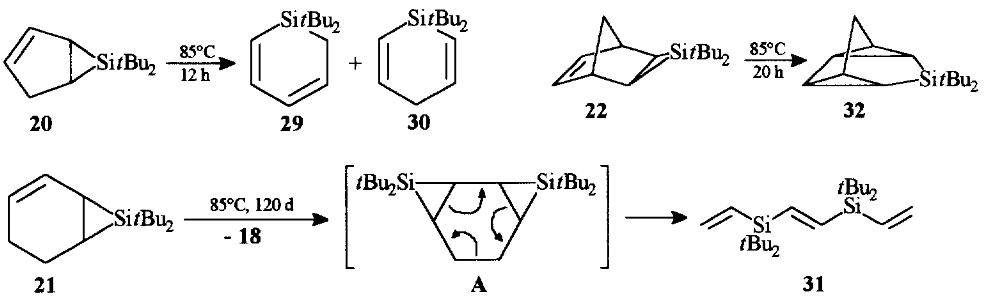


Fig. 1: Structure of **28** in the crystal (hydrogen atoms omitted, for crystallographic data see ref. 14)

While irradiation of the siliranes led to complex reaction mixtures, thermolyses proceeded more selectively: the three siliranes **20-22**, e.g., gave the products shown below in almost quantitative yields and without any side reactions.



20 **29** **30** **22** **32**

21 **A** **31**

The compounds **20** and **22** underwent rearrangement to the products **29**[16] and **30**[16] or **32**[16], respectively, in reactions which obey first order kinetics. In contrast, compound **21** underwent dissociation, presumably with formation of the silylene **2**, which reacted with a further molecule of the substrate to furnish the final product **31**[16] by way of the tricyclic intermediate **A**. None of the vinylsiliranes rearranged to [1+4] cycloadducts upon irradiation or thermolysis.

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4. Selected analytical data: **7**: ^{1}H NMR (300 MHz, C_6D_6): δ = 1.01, 1.13 (s; 18H, *t*Bu), 1.40-1.47 (m; 2H, CH), 1.85-2.02 (m; 4H, CH_2), 2.10-2.24 (m; 2H, CH_2). ^{13}C NMR (75.5 MHz, C_6D_6): δ = 19.34, 21.20, 21.45, 27.85, 29.85, 31.44, 33.91. MS: 210 (M^+). **10**: ^{1}H NMR (300 MHz, C_6D_6): δ = 0.35 (m; 1H, CH_2), 0.87 (m; 1H, CH_2), 0.99, 1.08 (s; 18H, *t*Bu), 1.15-1.25 (m; 1H, CH), 3.00 (m; 2H, CH_2), 7.11 (m; 1H, ar-H), 7.23 (m; 2H, ar-H), 7.32 (m; 2H, ar-H). ^{13}C NMR (75.5 MHz, C_6D_6): δ = 3.94, 14.51, 18.22, 19.02, 29.80, 30.72, 38.00, 125.82, 128.34, 128.45, 144.81. MS: 260 (M^+). **15**: ^{1}H NMR (300 MHz, C_6D_6): δ = 0.95 (AB-system; 1H, CH_2, ^{2}J = 12 Hz), 1.09 (s; 9H, *t*Bu), 1.15 (AB-system; 1H, CH_2, ^{2}J = 12 Hz), 1.25 (s; 9H, *t*Bu), 3.14, 3.25 (s; 6H, OCH_3), 4.06, 4.38 (AB-system; 2H, $=CH_2$). ^{13}C NMR (75.5 MHz, C_6D_6): δ = 7.55, 19.72, 19.93, 29.99, 30.70, 50.49, 54.36, 72.06, 84.04, 163.68. MS: 257 (MH^+). **21**: ^{1}H NMR (300 MHz, C_6D_6): δ = 0.99, 1.19 (s; 18H, *t*Bu), 1.25-1.40, 1.57-1.67 (m; 2H, CH), 1.90-2.21 (m; 4H, CH_2), 5.70-5.81, 6.05-6.12 (m; 2H, =CH). ^{13}C NMR (75.5 MHz, C_6D_6): δ = 11.72, 15.76, 19.14, 21.39, 21.64 , 24.38, 29.80, 31.74, 124.80, 128.40. MS: 222 (M^+). **22**: ^{1}H NMR (300 MHz, C_6D_6): δ = 0.78 (m; 2H, CH), 1.00, 1.17 (s; 18H, *t*Bu), 1.31 (m; 2H, CH_2), 3.19 (m; 2H, allyl-H), 6.24 (m; 2H, =CH). ^{13}C NMR (75.5 MHz, C_6D_6): δ = 19.63, 20.35, 26.20, 30.11 , 31.45, 43.95, 46.61, 137.10. MS: 234 (M^+).
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13. Selected analytical data: **26**: yellow crystals; 55% yield; mp.: 57°C; ^{1}H NMR (300 MHz, C_6D_6): δ = 0.71, 1.10 (s; 18H, *t*Bu), 1.24 (s; 4H, CH_3 + CH), 1.42 (d; 3H, CH_3, ^{3}J = 6.5 Hz), 2.58 (m; 1H, CH), 6.92, 6.98, 7.11 (m; 5H, ar-H). ^{13}C NMR (75.5 MHz, C_6D_6): δ = 15.44, 16.74, 20.19, 20.54, 25.15, 28.35, 29.23, 56.85, 120.09, 124.46, 128.92, 156.25, 196.77($\underline{C}$=N). ^{29}Si NMR (59.6 MHz, C_6D_6): δ = 30.35. **27**: yellow crystals; 34% yield; mp.: 85°C; ^{1}H NMR (300 MHz, C_6D_6): δ = 0.65 , 0.89 (s; 18H, *t*Bu), 1.42-1.95 (m; 6H, CH_2), 2.2-2.4 (m; 1H, CH), 3.10-3.25 (m; 1H, CH), 6.56, 7.92 (AA'BB'-system, 4H, ar-H). ^{13}C NMR (75.5 MHz, C_6D_6): δ = 18.85, 21.21, 25.79, 28.61, 28.76, 29.31, 32.80, 59.55, 119.56, 124.79, 144.81, 160.44, 202.64($\underline{C}$=N). MS: 358 (M^+). **28**: colourless crystals; 42% yield; mp.: 47°C; ^{1}H NMR (300 MHz, C_6D_6): δ = 0.84, 0.94 (s; 18H, *t*Bu), 1.24, 1.39, 1.98, 2.82, 3.05, 3.66 (m; 6H, CH + CH_2), 5.98, 6.28 (m; 2H, =CH), 6.88-7.18 (m; 5H, ar-H). ^{13}C NMR (75.5 MHz, C_6D_6): δ = 19.08, 22.51, 29.40, 29.57, 30.29, 44.66, 45.86, 49.87, 58.48, 119.66, 124.52, 128.91, 134.72, 141.99, 156.22, 197.13 ($\underline{C}$=N). MS: 337 (M^+).
14. Crystallographic data for compound **28** at 293 K: triclinic, $P\bar{1}$, Z = 4; a = 1045.6(2), b = 1405.5(3), c = 1462.6(2) pm, α = 76.81(1), β = 78.66(1), γ = 79.70(1)°, V = 2.0316(6) nm^3, ρ_{calc} = 1.107 g/cm^3, θ range: 1.50-23.02°, $Mo_{K\alpha}$, λ = 71.073 pm, 5988 reflections, 5591 independent, refinement on F^2 (SHELXL-93); final R1 ($F>4\sigma(F)$) = 0.0853, wR2 = 0.1691, residual electron density: 292 and -323 e/nm^3. Further details are deposited with the Cambridge Crystallographic Data Centre.
15. Silirane **24** was prepared according to the literature: see ref. 2.
16. Selected analytical data: **29**: a 2:1 mixture with **30** was obtained; 59% yield (GC); ^{1}H NMR (300 MHz, C_6D_6): δ = 0.96 (s; 18H, *t*Bu), 1.37 (m; 2H, CH_2), 5.82 (m; 2H), 6.74 (m; 2H). ^{13}C NMR (75.5 MHz, C_6D_6): δ = 7.97, 19.48, 27.97, 122.63, 126.66, 128.73, 142.72. ^{29}Si NMR (59.6 MHz, C_6D_6): δ = -5.12. GC-MS: 209 (MH^+). **30**: (1:2 mixture with **29**) 32% yield (GC); ^{1}H NMR (300 MHz, C_6D_6): δ = 1.04 (s; 18H, *t*Bu), 2.66 (m; 2H, CH_2), 5.91 (m; 2H), 6.62 (m; 2H). ^{13}C NMR (75.5 MHz, C_6D_6): δ = 19.11, 28.69, 34.61, 122.28, 146.11. ^{29}Si NMR (59.6 MHz, C_6D_6): δ = -17.53. GC-MS: 207 (MH^+ - H_2). **31**: colorless oil; yield: >95%; ^{1}H NMR (300 MHz, C_6D_6): δ = 1.09 (s; 36H, *t*Bu), 5.88, 6.07-6.25 (m; 6H; ABC-system), 7.00 (s; 2H; SiHC=CHSi). ^{13}C NMR (75.5 MHz, C_6D_6): δ = 19.30, 28.76, 133.44, 134.96, 148.64. ^{29}Si NMR (59.6 MHz, C_6D_6): δ = -6.45. MS: 364 (M^+). **32**: colourless oil; yield: >95%; ^{1}H NMR (300 MHz, C_6D_6): δ = -0.24 (m; 2H, SiCH), 1.16, 1.19 (s; 18H, *t*Bu), 1.42-1.54 (m; 2H), 1.63-1.74 (m; 1H); 1.75-1.83 (m; 2H), 1.90 (m; 1H). ^{13}C NMR (75.5 MHz, C_6D_6): δ = 8.02, 18.41, 20.81, 24.36, 27.46, 28.61, 29.46, 30.75. ^{29}Si NMR (59.6 MHz, C_6D_6): δ = 24.00. MS: 234 (M^+).

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