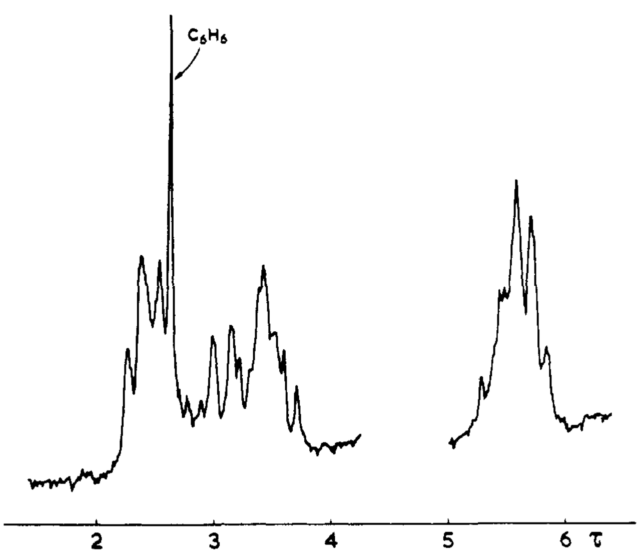
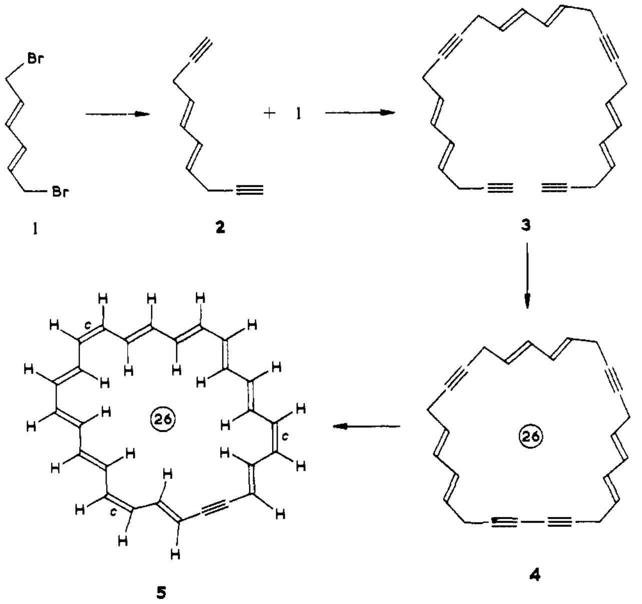


Figure 1. The 100-MHz spectrum of monodehydro[26]annulene (*e.g.*, **5**), measured in CD_2Cl_2 at −90°, using a time-averaged computer (internal standard, TMS).

yielded 65% of *trans,trans*-deca-4,6-diene-1,9-diyne (**2**) (see Scheme I): bp 51–53° (0.3 mm); mp 31–32°; mass spectrum *m/e* 130; $\lambda_{\max}^{\mathrm{EtOH}}$ 220 sh (ϵ 27,200), 227 (29,700), and 234 sh nm (23,300); nmr ($CDCl_3$, 60 MHz) τ 3.40–4.60 (m, 4, olefinic), 6.80–7.10 (m, 4, methylene), and 7.87 (t, 2, acetylenic). The diene-diyne **2** was treated with 1.1 mol equiv of ethylmagnesium bromide in tetrahydrofuran at room temperature, and then with 0.5 mol equiv of **1** in the presence of cuprous chloride[9] (boiling 1 hr). Chromatography on silica gel led to 10% of the C_{26} hexaenetetrayne **3**: mp 99–100°; nmr spectrum ($CDCl_3$, 60 MHz) τ 3.40–4.75 (m, 12, olefinic), 6.85–7.25 (m, 12, methylene), and 7.95 (t, 2, acetylenic). Substance **3** was very unstable and no mass spectrum could be obtained. The structure is based on the nmr spectrum and the fact that catalytic hydrogenation in tetrahydrofuran over platinum gave hexacosane (mass spectrum *m/e* 366).

Scheme I



Oxidative coupling of **3**, by dropwise addition of a solution in pyridine and tetrahydrofuran during 3.5 hr to cupric acetate monohydrate in pyridine at 72°,[4] gave ~2%[10] of the cyclic "monomer" **4** after chromatography on silica gel. The structure of **4** is based on the absence of terminal acetylene protons (nmr, ir) and the fact that catalytic hydrogenation as previously led to cyclohexacosane (mass spectrum *m/e* 364). Compound **4** was immediately subjected to rearrangement with a saturated solution of potassium *tert*-butoxide in *tert*-butyl alcohol (25°, 3 min). Chromatography on alumina (activity III) and then on silical gel gave monodehydro[26]annulene (*e.g.*, **5**) in ~3% yield as the sole highly colored substance. The compound formed dark purple rhombs from benzene–pentane (dark red in concentrated solution), which decomposed on attempted melting point determination: mass spectrum *m/e* 336.189 (calcd for $^{12}C_{26}{}^{1}H_{24}$: 336.188); $\lambda_{\max}^{\mathrm{ether}}$ 291 (ϵ 42,800), 370 (131,000), 386 (152,000), 439 (14,900), and 460 nm (15,900).[11] The monodehydro[26]annulene appeared to be homogeneous; *e.g.*, no separation occurred by chromatography on silica gel impregnated with 0.5% silver nitrate.[3] The monocyclic nature of the substance was confirmed by catalytic hydrogenation in tetrahydrofuran over platinum, which again led to cyclohexacosane (mass spectrum *m/e* 364).

The nmr spectrum of the monodehydro[26]annulene at −90° (Figure 1) consisted of complex multiplets at τ 2.1–3.8 and 5.2–6.0, the integrated areas being ~15:9.[12] The integration shows these bands to be due to the outer and inner protons, respectively, and indicates that the molecule contains 15 outer and 9 inner protons, as in **5**. However, the exact stereochemistry is unknown, and **5** is one of many possibilities. The fact that the inner protons resonate at considerably higher field than the outer protons clearly demonstrates the existence of a diamagnetic ring current, although this effect is less than in the lower homolog, monodehydro[22]annulene (outer protons, τ 1.55–3.75; inner protons, τ 6.55–9.30, at room temperature).[4]

Acknowledgments. We are indebted to the Royal Society for generous financial support.

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(10) This yield could not be improved by varying the conditions. It may be noted that *all-trans*-4,10,16,22-hexacosatetraene-1,7,13,19,25-pentayne, an isomer of **3**, could not be oxidized to the corresponding cyclic "monomer" (Y. Gaoni, C. C. Leznoff, and F. Sondheimer, *J. Amer. Chem. Soc.*, **90**, 4940 (1968)).

(11) The ϵ values are minimum ones, since the substance could not be dried thoroughly in view of its instability.

(12) The spectrum determined at room temperature was similar (τ 2.4–4.1 and 4.9–5.6), but was less well resolved.

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Syntheses and Photochemistry of 1,2,3-Trisilacycloheptane Derivatives. Precursors for Tailor-Made Organosilylenes

Sir:

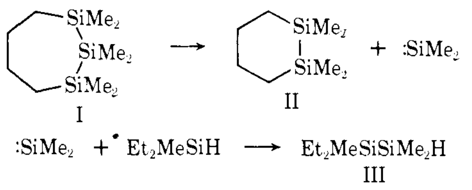
Recently, considerable attention has been devoted to the chemistry of divalent silicon compounds (silylenes).[1] A few methods used for preparation of organosilylenes have been developed, such as the reduction of halosilanes,[2] and the thermal decomposition of 7-silanorbornadienes[3] and polysilanes.[4] However, these systems are not always satisfactory for the study of silylenes since these systems require rather high temperature to generate silylenes. More recently, Ishikawa and Kumada[5] reported that dodecamethylcyclohexasilane underwent a ring-contraction reaction along with generation of dimethylsilylene on uv irradiation. This is a convenient system to produce the dimethylsilylene under mild conditions, but the structure of silylene thus obtained is still limited to the dimethyl derivatives.

In this report, we will describe syntheses of 1,2,3-trisilacycloheptane derivatives which were found to evolve silylenes on irradiation. The new system is advantageous as a precursor of silylenes in that the structure of silylene can be modified as described below, so that a tailor-made silylene can be generated easily under a mild condition.

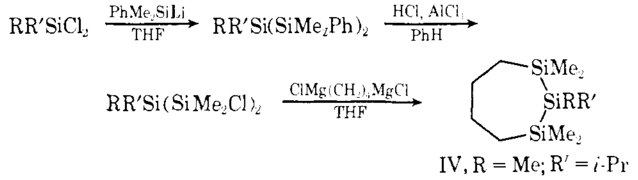
Addition of an ether solution of 1,3-dichlorohexamethyltrisilane[6] to a tetramethylene di-Grignard reagent in ether at room temperature afforded 1,1,2,2,3,3-hexamethyl-1,2,3-tisilacycloheptane (I) as an oil (bp 118–119° (31 mm); n^{20}D 1.5014; in 63.2% yield). Assigned structure is compatible with the spectral data of I: mass spectrum M$^+$ m/e 230; nmr[7] two singlets at δ 0.07 (12 H, CSiMeSi) and at 0.10 (6 H, SiSiMeSi), two multiplets at 0.68 (4 H, SiCH$_2$C) and at 1.56 (4 H, CCH$_2$C); uv (n-hexane) 221 nm (ϵ 6800).

Irradiation of I in n-hexane with a 160-W low-pressure mercury arc lamp under nitrogen atmosphere gave a single volatile product, which was identified as 1,1,2,2-tetramethyl-1,2-disilacyclohexane (II)[8] by comparison of spectral data and retention times on vpc with those of the authentic sample. Repeated runs indicate the yield of II based on the disappeared I to be nearly quantitative. The cyclic disilane, II, was fairly stable under the irradiation condition, but decomposed slowly by prolonged irradiation. Therefore, the yield of II depends on the period of irradiation, hence on the conversion rate. A typical example showed that the yield of II was 94.7% after irradiation for 12 hr, where the conversion of I to II was 56%.

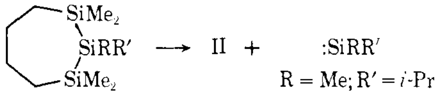
Formation of II on irradiation suggests that dimethylsilylene is generated from I at the same time. This was further evidenced by trapping of the silylene by a hydrosilane.[9] The n-hexane solution of I containing an excess amount of diethylmethylsilane was illuminated under the same condition for 30 hr. As a result, another product together with II was detected and was isolated by preparative vpc. Its structure was assigned to be 1,1,2-trimethyl-2,2-diethyldisilane (III) on the basis of its spectral data: mass spectrum M$^+$ m/e 170; ir 2134 cm^{-1} (Si–H); nmr a singlet at δ 0.03 (3 H, EtSiCH_3), a doublet at 0.12 (J = 4.8 Hz, 6 H, HSiCH_3), a multiplet at 0.46–1.06 (10 H, SiEt), and a septet at 3.65 (J = 4.8 Hz, 1 H, SiH). The yield of III was not quantitative, depending on the concentration of the trapping reagent. For example, in the presence of a 10 molar excess of diethylmethylsilane, III was obtained in 78.4% yield based on the amount of II.



Comparison of the bond energy of a silicon–silicon bond with that of a carbon–silicon bond may lead to the conclusion that the silicon atom involved in the silylene moiety may come from the central silicon atom of I. This is subsequently substantiated by the photolysis of 1,1,2,3,3-pentamethyl-2-isopropyl-1,2,3-trisilacycloheptane [IV: bp 113–123° (8 mm); uv (n-hexane) 215 nm (ϵ 8500); mass spectrum M$^+$ m/e 258; nmr two singlets at δ 0.08 (9 H, SiMe) and 0.15 (6 H, SiMe), three multiplets at 0.70 (4 H, SiCH$_2$C), 0.84–1.10 (7 H, Si-i-Pr), and 1.60 (4 H, CCH$_2$C)] prepared by the following scheme.[10]



Thus, photolysis of IV in the presence of diethylmethylsilane in n-hexane afforded exclusively II and a new disilane derivative, 1,2-dimethyl-2,2-diethyl-1-isopropyldisilane [V: nmr a singlet at δ 0.08 (3 H, EtSiCH_3), a doublet at 0.10 (J = 4 Hz, 3 H, HSiCH_3), and multiplets at 0.44–1.11 (10 H, SiEt), 0.85–1.11 (7 H, Si-i-Pr), and 3.46 (1 H, SiH)].



This fact indicates that variously substituted silylenes can be obtained by modifying the nature of the substituent on the central silicon atom of the cyclic trisilane, which may be prepared by the general scheme shown above. The studies on this line are now in progress in our laboratory and we are pleased to show an interesting example of a cyclic silylene generated from a unique spirotrisilane.

Addition of a tetrahydrofuran solution of phenyldimethylsilyllithium to 1,1-dichloro-1-silacyclopentane in tetrahydrofuran gave VI (bp 166–170° (0.35–0.40 mm), which was subsequently converted to VII (bp 104° (12 mm)) by the treatment of hydrogen chloride

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(1) For a pertinent review, see W. H. Atwell and D. R. Weyenberg, *Angew. Chem., Int. Ed. Engl.*, **8**, 469 (1969).

(2) P. S. Skell and E. J. Goldstein, *J. Amer. Chem. Soc.*, **86**, 1442 (1964).

(3) H. Gilman, S. G. Cottis, and W. H. Atwell, *ibid.*, **86**, 1596, 5584 (1964).

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(5) M. Ishikawa and M. Kumada, *ibid.*, 612 (1970).

(6) H. Sakurai, K. Tominaga, T. Watanabe, and M. Kumada, *Tetrahedron Lett.*, 5493 (1966).

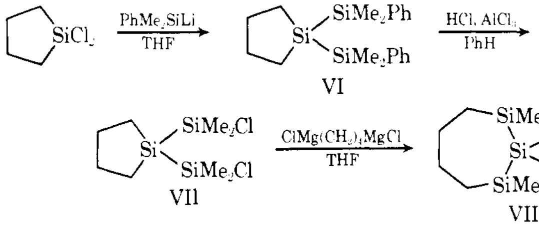
(7) All nmr spectra were measured at 100 MHz in CCl$_4$ solution containing a small amount of either C$_6$H$_6$ or CH$_2$Cl$_2$ as a field frequency lock. Chemical shifts are given in δ value relative to either internal C$_6$H$_6$ or CH$_2$Cl$_2$ taken as δ 7.26 or 5.30, respectively.

(8) M. Kumada, K. Tamao, I. Takubo, and M. Ishikawa, *J. Organometal. Chem.*, **9**, 43 (1967).

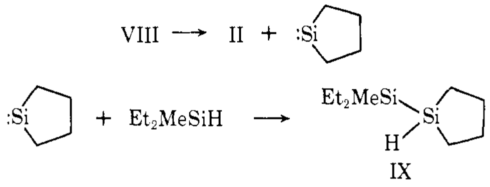
(9) Hydrosilanes are known as an efficient trap of silylenes.[2,4d,5]

(10) All new compounds gave satisfactory elemental analyses.

in the presence of aluminum chloride in benzene. Then, a tetrahydrofuran solution of VII was treated with tetramethylene di-Grignard reagent and this gave 5,6,11-trisilaspiro-4,6-undecane (VIII) as an oil (bp 97–98° (1 mm)). The assigned structure is in accord with spectral data of VIII: mass spectrum M^+ 256; nmr a singlet at δ 0.11 (12 H, SiMe), two multiplets at 0.77 (8 H, $SiCH_2C$) and 1.59 (8 H, CCH_2C); uv (in n-hexane) 219 nm (ϵ 8700).



Irradiation of an n-hexane solution of VIII containing a 10 molar excess amount of diethylmethylsilane as a trapping agent by a 160-W low-pressure mercury arc lamp for 20 hr afforded II and a new product, the yield of II being 80–90%. The latter product was isolated by preparative vpc and its structure was elucidated to be IX from its nmr spectrum: a singlet at δ 0.06 (3 H, SiMe), multiplets at 0.50–1.10 (14 H, SiEt, $SiCH_2C$), and at 1.58 (4 H, CCH_2C), and a quintet at 3.60 (J = 4.6 Hz, 1 H, SiH). The disilane IX should arise from the insertion of the cyclic silylene to the Si–H bond of diethylmethylsilane. Thus, the cyclic silylene was found to undergo normal insertion reaction into a silicon–hydrogen bond like the dimethylsilylene.



Related works are in progress and will be reported elsewhere.

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Some Unusual Anion Effects on the Rate of Reduction of Iron(III) Complexes[1]

Sir:

Electron transfer to the iron atom in cytochrome c can occur either directly or *via* the edge of the porphyrin ring system.[2,3] Electron transfer to the iron atom *via* the tyrosine residues of the polypeptide chain has also been proposed.[4,5] In an attempt to distinguish between these pathways, we are studying the effect of anions on the rate of reduction of cytochrome c^{III} by chromium(II).[6] In the course of this work, we observed that the reduction of cytochrome c^{III} by chromium(II) is markedly catalyzed by thiocyanate ions under conditions where chloride ions have a negligible effect. We now wish to report the results of a study of the effect of anions on the rate of reduction of the tris(1,10-phenanthroline) and the tris(2,2′-bipyridine) complexes of iron(III) by ferrous ions (eq 1). These effects are compared with those previously observed on the Fe^{3+}–Fe^{2+} reaction (eq 2).

$$\mathrm{Fe(phen)_3^{3+} + Fe^{2+} \longrightarrow Fe(phen)_3^{2+} + Fe^{3+}} \tag{1}$$

$$\mathrm{Fe^{3+} + Fe^{2+} \rightleftharpoons Fe^{2+} + Fe^{3+}} \tag{2}$$

The oxidation–reduction reactions were studied on the stopped-flow apparatus previously described.[7] The kinetics of the reactions were determined under pseudo-first-order conditions, with the ferrous ions present in excess. In most of the runs the formation of the iron(II) complex was followed at its absorption maximum in the visible region of the spectrum (510–529 nm); in some instances, the disappearance of the iron(III) complex was also followed (591–617 nm). Except where noted, the reactions were studied in 1.0 M perchloric acid at 25.0°.

Values of k_0 and of k_1 defined by eq 3 and 4 (where X^- represents the added anion) are presented in Table I, which also contains data on the effect of anions on the reduction of Fe^{3+} by Fe^{2+} ions. It is evident from the rate constants presented in this table that

Table I. Comparison of the Effect of Anions on the Reduction of Iron(III) Complexes by Ferrous Ions in 1.0 M Perchloric Acid at 25.0°

Iron(III) complex	X^-	k_0, M^{-1} sec^{-1}	k_1, M^{-2} sec^{-1}	Ref
$Fe(phen)_3^{3+}$		3.40×10^4		*a*
$Fe(phen)_3^{3+}$	Cl^-		4.9×10^5	*a*
$Fe(phen)_3^{3+}$	Br^-		3.8×10^5	*a*
$Fe(phen)_3^{3+}$	I^-		2.4×10^8	*a*
$Fe(phen)_3^{3+}$	N_3^-		8.1×10^8	*a, b*
$Fe(phen)_3^{3+}$	SCN^-		2.0×10^9	*a*
$Fe(bipy)_3^{3+}$		1.88×10^4		*a*
$Fe(bipy)_3^{3+}$	Cl^-		2.9×10^5	*a*
$Fe(bipy)_3^{3+}$	SCN^-		8.9×10^8	*a*
$Fe(dimbipy)_3^{3+\,c}$		0.032×10^4		*a*
$Fe(dimbipy)_3^{3+\,c}$	Cl^-		7.4×10^3	*a*
$Fe(dimbipy)_3^{3+\,c}$	SCN^-		3.8×10^7	*a*
Fe^{3+}		3.0		*d, e*
Fe^{3+}	Cl^-		87	*d, e, f*
Fe^{3+}	N_3^-		7.1×10^7	*d, g*
Fe^{3+}	SCN^-		2.4×10^3	*d, f, h*

[a] This work. [b] Medium was a 1 M NaN_3–$NaClO_4$–$HClO_4$ mixture. [c] The ligand is 4,4′-dimethyl-2,2′-bipyridine. [d] Ionic strength = 0.55 M, temperature = 20°. [e] J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952). [f] This reaction proceeds by parallel inner- and outer-sphere paths. [g] D. Bunn, F. S. Dainton, and S. Duckworth, *Trans. Faraday Soc.*, **57**, 1131 (1961). [h] R. A. Horne, Ph.D. Thesis, Columbia University, 1955.

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(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

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