at the HMO level), but the exchange integral, which favors the T state energetically, should also be larger (cf. the larger value of D). The hyperfine coupling constant for the methylene protons is isotropic as expected and of the right order of magnitude (using Hückel spin densities and standard relations,¹⁰ one expects $a \approx (1/2) (3/\sqrt{26} + 3/\sqrt{26})^2 \times 42.6 \times \cos^2 30^\circ$ = 22 (G).

The UV-vis absorption spectrum of III is one of the very few ever recorded for the singlet state of an even conjugated hydrocarbon without a classical valence structure.¹¹ It is strikingly different from the spectra of ordinary alternant hydrocarbons in that it contains a long succession of very weak absorption bands at long wavelengths. It is in fair agreement with our PPP calculation which suggests that there is an additional forbidden transition near 9000 cm⁻¹ and that the observed fluorescence is of the $S_2 \rightarrow S_0$ type. Our attempts to locate this predicted transition in the near-IR region failed.

2,3 shifts in 1,3 biradicals have been frequently discussed, e.g., in the thermal rearrangement of cyclopropanes to propenes,¹² and in their photochemical interconversion.¹³ We believe that ours is the first direct observation of a 2,3-hydrogen shift in a 1,3 biradical, and indeed of the whole sequence commonly postulated¹³ in the photochemical process arylcyclopropane \rightarrow (*hv*) 1,3 biradical \rightarrow (Δ) arylpropene (at 20 °C, irradiation of I smoothly produces II).

The expected relative ease of 2,3 shifts in 1,3 biradicals is usually attributed to the partial development of the 1,2 double bond as the transition state is reached. This argument holds only for the S_0 state; such assistance is missing in T_1 state and in the lowest excited singlet state S_1 , in which the reactions are more nearly thermoneutral. Naively, one could expect the reaction to be facile in the "zwitterionic"^{3,14} S₁ state, in which it can be approximately described as a 2,3 shift in a carbonium ion carrying a carbanion substituent (carbon 1) (eq 1). These

$$\begin{array}{c} \overset{H}{\xrightarrow{}} \overset{H}{\xrightarrow{}$$

qualitative notions and the resulting expectation of an increase in the activation energy for the shift in the order $S_1 < S_0 < T_1$ are supported qualitatively by approximate calculations for the 1,3-trimethylene biradical -> propene rearrangement which we have performed at the STO-3G SCF + 3×3 CI level, with considerable but not exhaustive geometry optimization.

Accordingly, we would expect the thermal transformation III \rightarrow (Δ) II to involve the S₀ state of III and a nonvanishing activation energy, and the photochemical transformation III \rightarrow (hv) II to occur for that fraction of excited molecules which reaches the very low lying S_1 state, with little or no activation energy.

The presently available photochemical results are compatible with these expectations if we postulate that the calculated very weak $S_0 \rightarrow S_1$ transition in the infrared is too weak to be observed against the background of solvent overtones and that a radiationless $S_2 \rightarrow S_1$ process competes with $S_2 \rightarrow S_0$ emission (such emission is plausible in view of the large calculated S_2-S_1 gap). However, the frequency factor of the thermal reaction III \rightarrow II is abnormally low and suggests that the reaction involves either tunneling or a spin-forbidden process such as might result from the presence of a large barrier in the S₀ and a small one in the T_1 surface. We wonder, however, whether the temperature dependence of the reaction rate does not reflect as much the properties of the glass as those of the isolated molecule even for a possibly simple monomolecular

process such as III \rightarrow II. E.g., over the temperature range used (119-133 K), the viscosity of 1-pentanol changes by a factor of 3×10^4 . Similar huge changes also occur for other glasses over the temperature region in which they are transparent and stable. Some curious variations in the frequency factor for the rate of disappearance of trimethylenemethane in glasses were reported recently.¹⁵ Clearly, now that the agreement of the optical and ESR kinetic data for III in 1-pentanol has been demonstrated, it will be necessary to perform ESR studies, which do not require good transparency, in a large number of glasses, and also to explore isotope and substituent effects.

Barriers to ring closure in 1,3 biradicals are of considerable current interest.¹⁵ The absence of competing thermal conversion III \rightarrow I shows that in rigid 1-pentanol the barrier is considerable in the case of III. Since the ring closure requires a larger geometry change than the hydrogen shift, extrapolation to gas phase is not straightforward. Also, the presence of the rigid and conjugating naphthalene unit is undoubtedly unfavorable for ring closure.

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Silacyclobutenes: A Simple Synthesis¹

Sir:

Silacyclobutenes have been largely ignored during the recent surge of interest in the preparation and reactions of strainedring organosilicon compounds.² This neglect, which seems

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Table I. Silacyclobutenes Prepared by Flash Vacuum Pyrolysis of Diallylic Silanes

	-	Silacyclobutene		
Entry	Reactant	Structure (yield) ^a	IR: C==C (cm ⁻¹)	¹ H and ¹³ C NMR ^b
1	$(CH_2 = CHCH_2)_2Si(CH_3)_2$	□_{Si(CH,),2}(25%) 3	1511 (m)	¹ H: δ 0.33 (s, 6 H, CH ₃), 1.55 (d, 2 H, J = 1.8 Hz, CH ₂), 6.27 (d, 1 H, J = 7.3 Hz, CHSi), 7.16 (d of t, 1 H, J = 1.8, 7.3 Hz,CH); ¹³ C: δ_{C} 0.83 (CH ₃), 22 (CH ₂), 142 (CHSi), 152 (CH)
2	$(CH_2 = C(CH_3)CH_2)_2Si(CH_3)_2$	(36%) Si(CH ₄) ₂ 4	1580 (m) ^c	¹ H: $\delta 0.27$ (s, 6 H, Si-CH ₃), 1.38 (m, 2 H, CH ₂), 1.87 (m, 3 H, C-CH ₃), 5.70 (m, 1 H, ==CHSi); ¹³ C: δ_{C} -1.46 (Si-CH ₃), 23.1, 24.1 (CH ₂ and CH ₃ on C; assignment not made), 132.1 (==CHSi) ^d
3	Si(CH ₂ CH=CH ₂) ₂	5 5	1507 (m)	¹ H: δ 0.7-1.0 (m, 4 H, CH ₂ CH ₂ Si), 1.5-1.8 (m, 6 H, CH ₂ CH ₂ Si + SiCH ₂ CH=), 6.09 (d of t, 1 H, J = 7.1, 0.7 Hz, =-CHSi), 7.12 (d of t, 1 H, J = 7.1, 1.9 Hz, =-CH); ¹³ C: δ _C 11.9 (CH ₂ CH ₂ Si), 21.5, 26.5 (other CH ₂ carbons; assignment not made), 139.3 (=-CHSi), 152.9 (=-CH)
4	Si(CH ₂ CH=CH ₂) ₂		1510 (m)	¹ H: $\delta 0.89$ (t, 4 H, $J = 6$ Hz, CH ₂ CH ₂ Si), 1.3-1.9 (m with d of d at 1.53, $J = 1.95$, 0.49 Hz, 8 H; other CH ₂ protons with CH ₂ CH= at 1.53), 6.16 (d of t, 1 H, $J =$ 0.7, 7.3 Hz, =CHSi), 7.12 (d of t, 1 H, $J =$ 1.8, 7.1 Hz, =CH); ¹³ C: δ_{C} 14.7, 20.9, 24.9, 29.7 (CH ₂ carbons), 140.5 (=CHSi), 152.1 (=CH)

^a Yields determined by NMR or GC analysis. ^b All ¹³C spectra determined in CDCl₃ solution except for that of **3** which was used neat; the ¹H spectra were determined in CCl₄ (silacyclobutenes **3** and **4**) or CDCl₃ (silacyclobutenes **5** and **6**). ^c Note that 3-methyl-1,1,2,2-tetrafluoro-1,2-disilacyclobut-3-ene also has a C=C band at 1580 cm⁻¹: C. S. Liu, J. L. Margrave, and J. C. Thompson, *Can. J. Chem.*, **50**, 465 (1972). ^d Under the FT NMR conditions employed, the quaternary olefinic carbon was not seen.

surprising in view of the rich chemistry associated with cyclobutenes,³ may be due to the general rarity of silacyclobutenes. To date only silacyclobutenes ring-substituted with aryl groups have been synthesized and these by multistep procedures.^{2d} We now wish to report a simple one-step synthesis of silacyclobutenes which makes available for study a wide range of these compounds including those unsubstituted on the ring.

This synthesis was discovered during an attempt to examine by flash vacuum pyrolysis (FVP) spectroscopic techniques^{1a} silabutadienes (e.g., 2) which we hoped to generate through retro-ene reaction⁴ of diallylsilanes such as 1 (eq 1). In the



event, initial study of the FVP of 1 (utilizing a pyrolysis system connected directly to the source of a mass spectrometer^{1a}) suggested the clean decomposition of 1 to species of formulas $C_5H_{10}Si$ (*m/e* 98) and C_3H_6 (*m/e* 42) in the gas phase beginning at temperatures of ca. 600 °C. Repetition of the pyrolysis on a preparative scale using a 2 × 68 cm quartz tube filled with

porcelain Berl saddles⁵ and heated in a tube furnace at 710 °C with a sample flow rate of 3 ml/h at ca. 0.01 mm⁶ gave 1,1dimethylsilacyclobutene (3) (25% yield; 41% yield based on unrecovered 1), propylene (22% yield based on isolation of 1,2-dibromopropane), diallyldimethylsilane (1) (55% recovery), and a number of minor products as indicated by GC analysis. Starting material 1 could be recovered by distillation and pyrolyzed again to give additional 3. Silacyclobutene 3, showing a GC retention time nearly identical with that of authentic 1,1-dimethylsilacyclobutane,⁷ had bp 70-71 °C.⁸ High resolution mass spectrometry indicated a parent ion at m/e98.05510 (base peak; calcd for C₅H₁₀Si 98.05510) with prominent peaks corresponding by exact mass to $P - CH_3$ (93%), C₃H₉Si (47%), and C₃H₈Si (28%). Gas-phase IR showed bands at 3065 (m), 3019 (w), and 1511 cm⁻¹ (m) among others (all bands absent from the IR spectrum of 1,1-dimethylsilacyclobutane); ¹H NMR (CCl₄) showed δ 0.33 (s, 6 H), 1.55 (d, 2 H, J = 1.8 Hz), 6.27 (d, 1 H, J = 7.3 Hz),and 7.16 (d of t, 1 H, J = 1.8, 7.3 Hz); ¹³C FT NMR showed $\delta_{\rm C}$ 0.83 (q, J = 120 Hz), 22 (t, J = 131), 142 (d, J = 170 Hz), and 152 (d, J = 168 Hz); ²⁹Si NMR showed $\delta_{Si} - 9.6$ ppm (proton decoupled; upfield from tetramethylsilane). The IR band at 1511 cm⁻¹ may be identified as the C=C stretch; the long wavelength position is fully consistent with the data for cyclobutane (C=C at 1566 cm⁻¹)¹⁰ and the "conjugative" effect of silicon. The ¹H NMR spectrum of 3 is in excellent agreement with the data reported for aryl-substituted silacyclobutenes.^{2d,11} The ¹H and ¹³C NMR results are also consistent with literature values for related systems^{2b,3} including 1-silacyclopent-2-enes.¹² The ²⁹Si NMR peak position shows none of the dramatic shielding associated with silacyclopropanes and silacyclopropenes.26

Additional examples of the synthesis of silacyclobutenes by

pyrolysis of diverse diallylic silanes are indicated in Table I along with selected spectral data for these new compounds.¹³ The requisite precursors¹³ are readily prepared through reaction of appropriate Grignard reagents and dichlorosilanes.¹⁴ The synthesis can be applied to spirosilacyclobutenes as well as silacyclobutenes variously substituted on the ring or at silicon, with some limitations. Thus, pyrolysis of diallylsilane itself at 710 °C led to a very complex mixture of products while diallyldimethoxysilane passed through the pyrolysis system unscathed at 710 °C.

A careful GC-MS study of the products from pyrolysis of 1 indicated the absence of 1,5-hexadiene (derived from combination of allyl radicals). This observation argues against significant contributions from a free radical mechanism¹⁵ such as that depicted in eq 2. However, additional kinetic studies would be desirable to confirm the mechanism proposed in eq 1 and provide activation parameters for comparison with retro-ene reactions involving first-row elements. In light of our findings it would also be desirable to reexamine the pyrolysis of allyltrimethylsilane, a reaction whose mechanism has been the subject of controversy.¹⁶ It is clear that the FVP of diallylsilanes represents a valuable new route to silacyclobutenes while the retro-ene reaction of suitably functionalized allylsilanes merits further study as a pyrolytic route to other silaolefinic compounds. We shall report separately on the chemistry of silacyclobutenes and on our efforts to obtain direct spectroscopic evidence for silabutadienes.

$$(CH_2 = CHCH_2)_2Si(CH_3)_2 \xrightarrow{\Delta} CH_2 = CHCH_2\dot{S}i(CH_3)_2$$

$$1 + CH_2 = CHCH_2\dot{S}i(CH_3)_2$$

 $CH_2 = CHCH_2 + 1$ $\rightarrow CH_2 = CH\dot{C}HSi(CH_3)_2CH_2CH = CH_2$ $+ CH_2 = CHCH_3$

$$CH_{2} = CHCHSi(CH_{3})_{2}CH_{2}CH = CH_{2} \rightarrow CH_{2} = CHCH_{2}$$
$$+ CH_{2} = CHCH = Si(CH_{3})_{2}$$
$$2$$
$$2 \rightarrow 3$$
(2)

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Complete Substitution of Carbonyl Groups in Cyclopentadienyliron Dicarbonyl Dimer by Methylaminobis(difluorophosphine). A Novel Bridging CH₃NPF₂ Ligand Bonded to Metals through Both Phosphorus and Nitrogen

Sir:

Recently we have reported unusual products obtained by reactions of the bidentate ligand $CH_3N(PF_2)_2^1$ with a variety of metal carbonyls and their derivatives including M(CO)₆ (M = Cr, Mo, and W),² Fe(CO)₅,³ Fe₂(CO)₉,³ Fe₃(CO)₁₂,^{3,4} Co₂(CO)₈,⁵ and C₅H₅V(CO)₄.⁶ This communication reports the pairwise substitution of the four carbonyl groups in $[C_5H_5Fe(CO)_2]_2$ to give successively the dicarbonyl $[C_5H_5FeCO]_2(PF_2)_2NCH_3$ and the carbonyl-free complex $[C_5H_5Fe(PF_2)_2NCH_3]_2$. The carbonyl-free complex is of more than routine interest since x-ray crystallography indicates an unexpected structure containing a bridging CH₃NPF₂ ligand bonded to one iron atom through nitrogen and to the other iron atom through phosphorus. The complex $[C_5H_5Fe(PF_2)_2$ - NCH_{3} is thus the first example of a transition metal complex in which an aminodifluorophosphine-derived ligand⁷ is bonded to a transition metal through nitrogen as well as phosphorus.

The complexes⁸ [C₅H₅FeCO]₂(PF₂)₂NCH₃ (purple crys-