for 10 min. The ether layer was transferred to a 25-mL round-bottomed flask, and the water layer was extracted with ether (3 × 5 mL) by stirring. The combined ether extracts were dried over $MgSO_4$ and then passed through $MgSO_4$. The solvents were removed, and the crude residue was purified by pipet flash chromatography using hexane/ethyl acetate (90:10) to give 13.5 mg, (95.8%, 44.8 mCi) of tritiated fluoro diene **8b** (specific activity = 0.94 Ci/mmol).

[12-^{3}H]-12-Fluoro-(*Z*,*Z*)-dodeca-3,6-dien-1-ol ([12-^{3}H]-8). To a solution of tritiated THP fluoro diene **8b** (13.5 mg, 0.048 mmol, 0.943 Ci/mmol) in dry ethanol (3 mL) was added pyridium *p*-toluenesulfonate (PPTS, 2 mg, 0.008 mmol), and the mixture was gently refluxed overnight. After cooling to room temperature, the ethanol was removed, the residue was diluted with ether (5 mL), and the ether solution was washed with saturated $NaHCO_3$ (1 mL) by stirring. The ether layer was then transferred to a 25-mL round-bottomed flask, the water layer was extracted with ether (3 × 5 mL), and the combined extracts were dried over $MgSO_4$. The solution was then passed through $MgSO_4$, the solvent was removed, and the crude product was purified by pipet flash chromatography using hexane/ethyl acetate (80:20) to yield 6.9 mg (71.8%, 34.2 mCi) of the tritiated fluoro dienol 8, (specific activity 0.99 Ci/mmol).

[12-^{3}H]-12-Fluorododecanol (25). A solution of the tritiated fluoro dienol 8 (2.0 mg, 0.01 mmol) in absolute ethanol (1 mL) was placed in a 10-mL round-bottomed flask containing 1 mg of 10% Pd/C and a stir bar. The flask was connected to a three-way stopcock adaptor equipped with a ballon. The system was evacuated and filled with hydrogen (1 L), and the mixture was stirred overnight. GC analysis (DB-5 fused silica, 30 m × 0.25 mm, 100–200 °C, 2 °C/min) indicated the reaction to be complete. The reaction mixture was filtered through silica gel, and the solvent was removed to give the saturated dienol **25** (99%, 10 mCi) (specific activity = 1.0 Ci/mmol).

[12-^{3}H]-(*Z*,*Z*)-Dodeca-3,6-dien-1-ol ([12-^{3}H]-7). To a solution of tritiated THP dienol **20** (14.0 mg, 0.050 mmol, 1 equiv) and triethylamine (100 μL of a 96.2 μL/mL solution, 0.070 mmol, 1.4 equiv) in methylene chloride (2 mL) cooled to 0 °C was added methanesulfonyl chloride (100 μL of a 50.0 μL/mL solution, 0.065 mmol, 1.3 equiv). The mixture was stirred at ice-bath temperature for 4 h, diluted with ether (10 mL), and washed with water (2 mL) by stirring. The organic layer was transferred to a round-bottomed flask, the water layer was extracted with ether (3 × 5 mL), and the combined organics were dried over $MgSO_4$. The solution was then passed through $MgSO_4$, and the volatiles were removed. The residue was diluted with dry ether (3 mL), and lithium aluminum hydride (2 mg, 0.050 mmol, 4 equiv) was added. The mixture was stirred for 1 h at room temperature, and then 2 N sodium hydroxide (4 drops) was added. After being stirred for 5 min, the mixture was further diluted with ether (3 mL) and 2 N NaOH (1 mL), the ether layer was removed, and the water layer was extracted with ether (3 × 3 mL). The combined organics were dried over $MgSO_4$, and the solvent was removed. The crude material was purified by pipet flash chromatography using hexane/ethyl acetate (95:5) to give 11.9 mg (90.0%, 55.3 mCi) of the tritiated THP ether (specific activity = 1.24 Ci/mmol).

Deprotection with PPTS as described above gave the crude dienol, which was purified by pipet flash chromatography using hexane/ethyl acetate (83:17) to give 5.2 mg (63.3%, 28.9 mCi) of the tritiated dienol **7** (specific activity = 1.20 Ci/mmol).

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Registry No. **2**, 32451-95-9; **2**-yne, 55182-73-5; **3**, 68892-27-3; **3**-yne, 55182-74-6; **4**, 88730-45-4; **4** (THP ether), 88730-46-5; **5**, 88730-47-6; **5** (THP ether), 88730-48-7; **5**-yne, 88730-68-1; **6**, 88730-49-8; **6** (THP ether), 88730-50-1; **7**, 29125-78-8; [12-^{3}H]-**7**, 88730-51-2; [12-^{3}H]-**7** (THP ether), 88730-52-3; **8**, 88730-53-4; **8** (THP ether), 88730-54-5; [12-^{3}H]-**8**, 88746-43-4; **8b**, 88730-55-6; **9**, 40365-61-5; **10a**, 111-83-1; **10b**, 112-29-8; **11a**, 373-28-4; **11b**, 593-12-4; **11c**, 334-61-2; **12a**, 87641-52-9; **12b**, 88730-56-7; **13a**, 88746-44-5; **13b**, 88730-57-8; **13c**, 88730-58-9; **14**, 51721-39-2; **15**, 1549-82-2; **16**, 2886-59-1; **17**, 88730-59-0; **17** (methyl ester alcohol), 38341-83-2; **17** (THP ether alcohol), 88730-60-3; **18**, 88730-61-4; **18**·PPh_3, 88730-62-5; **19**, 34067-76-0; **20**, 88730-63-6; [12-^{3}H]-**20**, 88730-64-7; **21**, 20739-58-6; **22**, 18495-27-7; **23a**, 88730-65-8; **23b**, 65090-68-8; **24**, 88730-66-9; [12-^{3}H]-**25**, 88730-67-0; $Br(CH_2)_8OH$, 50816-19-8; $Br(CH_2)_{10}OH$, 53463-68-6; $Br(CH_2)_6OH$, 4286-55-9; $HC{\equiv}C(CH_2)_8OH$, 17643-36-6; $CH_3(CH_2)_4CHO$, 66-25-1; 6-hexanolactone, 502-44-3.

Electrophilic Cleavage of 1-Allyl-1,2,5-trimethyl-1-silacyclopentane. Stereochemistry at Silicon

Fritz Franke, Matthew J. Cuthbertson, and Peter R. Wells*

Chemistry Department, University of Queensland, Brisbane 4067, Australia

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The preparation of mixtures of the isomers of 1-allyl-1,2,5-trimethyl-1-silacyclopentane and some of their reactions with electrophiles are described. Individual isomers and reaction products have not been isolated but have been characterized by ^{1}H and ^{13}C NMR spectroscopy. Cleavage of the allyl group may proceed with retention, inversion, or loss of configuration at silicon according to the reagent employed.

We have previously described the synthesis, separation and characterization of the stereoisomers of 1,2,5-trimethyl-1-silacyclopentane and have illustrated the use of substrates derived from this system in stereochemical studies.[1,2] These results suggest that the system might be well suited to the examination of the stereochemical consequences at silicon of the electrophilic cleavage of allyl groups and provide definitive information on the mechanism of this reaction.

Allylic silanes are of considerable synthetic importance by virtue of their reactivity towards a variety of electrophiles and the regioselectivity of the processes.[3] Allylic

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Table I. ^{13}C Chemical Shift of 1-Allyl-1,2,5-trimethyl-1-silacyclopentanes[a]

	E,Z/Z,E	E,E	Z,Z[b]
$SiCH_3$	−7.11	−9.56	(−5.35)
CCH_3	15.65; 15.20	15.88	(15.3)
C_2,C_5	21.68; 19.62	18.25	(20.8)
C_3,C_4	35.74; 35.55	34.35	(33.4)
C_α	20.46	22.87	?
C_β	134.87	134.96	?
C_γ	113.03	112.76	(113.3)

[a] In ppm relative to internal Me_4Si. [b] Results obtained from the examination of one spectrum only.

rearrangement is observed in almost all cases, and this may be the result of an S_E2' mechanism, which is suggested to be operative in the case of allylstannanes.[4] Alternatively it may be argued that the reaction proceeds through addition yielding a cation stabilized by the β-trialkylsilyl group followed by elimination of the trialkylsilyl moiety.[5] Supportive of this view is the report that products of addition to the C=C can be isolated in some cases of reactions of electrophiles with allyltrimethylsilane.[6]

Clearly information on the stereochemical outcome of these reactions for both the entering and leaving groups will be valuable for mechanistic and synthetic purposes. The present study is concerned with the latter.

Results and Discussion

Several preparations of 1-allyl-1,2,5-trimethyl-1-silacyclopentane were carried out employing various samples of the chloro compound[2] with isomeric compositions varying from almost pure *E,Z/Z,E* to mixtures rich in the *E,E* or in the *Z,Z*- isomers. Yields after purification were far from quantitative and the final products were generally mixtures of the *E,Z/Z,E* and *E,E* isomers of the allyl derivative, except that only the *E,Z/Z,E* product is obtained from the *E,Z/Z,E* chloro compound. On one occasion, however, a product comprised of *E,Z/Z,E*:*Z,Z*:*E,E* = 46:33:21, as judged by ^1H NMR of the Si–Me region, was obtained from chloro compound having *E,Z/Z,E*:*E,E*:*Z,Z* = 49:31:21. This suggests that the reaction follows the anticipated[7] course giving inversion of configuration at silicon. The low yields of *Z,Z*-allyl derivative in most of our preparations could arise from the lower reactivity of the more hindered *E,E*- chloro compound and/or from preferential losses in our workup procedures.

Analysis of these preparations is readily accomplished by means of ^{13}C and ^1H NMR spectroscopy and by gas chromatography. However the latter technique, although more convenient does not give a separate peak for the *Z,Z*-isomer which lies under that for the *E,Z/Z,E* isomer. Correction using ^1H NMR data is quite simple. The ^{13}C chemical shift data are given in Table I. The assignments of configuration are based upon the highest field Si–CH_3 being that of the *E,E* isomer due to shielding by the adjacent C–CH_3 groups and the lowest field Si–CH_3 being that of the *Z,Z* isomer. The Si–CH_3 of the *E,Z/Z,E* isomer is at an intermediate shift position. (This latter configuration will already have been assigned from the observation of pairs of resonances for the silacyclopentane carbons). In similar fashion the C_α resonance of the *E,E* isomer is

Table II. ^1H NMR Spectra of 1-Allyl-1,2,5-trimethyl-1-silacyclopentanes[a]

	E,Z/Z,E	E,E	Z,Z
Si-CH_3	−0.01 (s)	−0.03 (s)	0.06 (s)
C-CH_3	0.99 (d, J = 6.6 Hz)		
	1.04 (d, J = 7.1 Hz)		
α-CH_2	1.56 (d, J = 8.0 Hz, of t, J = 1.3 Hz)		
β-CH	5.79 (m)		
γ-CH_2	4.85 (m)		
H_2-H_5	1.0-2.0		

[a] Chemical shifts in ppm relative to internal Me_4Si.

Table III. HCl Cleavage of 1-Allyl-1,2,5-trimethyl-1-silacyclopentane

	composition of initial allyl[a]				composition of chloro product[b]		
expt no.	E,Z/Z,E	Z,Z	E,E	extent of react, %	E,Z/Z,E	E,E	Z,Z
1	54	15	31	100	54	16	30
2	60	0	40	30	67	2	32
3	51	10	39	80	64	17	39
4	47	10	43	100	49	11	40
5	48	10	42	50	52	9	39
6	60	3	37	90	62	3	35

[a] By GC and ^1H NMR. [b] By GC (see ref 2).

to low field of that in the *E,Z/Z,E* isomer and the corresponding resonance of the *Z,Z* isomer would be expected to be further to high field although it could not be located with certainty. Several mixtures of *E,E* and *E,Z/Z,E* isomers were available allowing the resonances of the individual isomers to be recognized, but only one product had the *Z,Z* isomer in substantial amount. Details of the ^1H NMR spectrum of the *E,Z/Z,E* isomer are given in Table II with the Si–CH_3 chemical shifts only given for the other isomers. The spectra of the mixtures were too complex to allow the assignment of resonances other than the high-field singlets, but these again serve to characterise the three isomers. In both the ^1H and the ^{13}C spectra the allyl group shows much the same set of chemical shifts as are found for allyltrimethylsilane.[8]

	Me_3Si—CH_2—CH=CH_2			
^1H, ppm	0.00	1.48	5.77	4.78, 4.80
^{13}C, ppm	−2.2	24.6	134.9	112.5

In the *E,Z/Z,E* isomer the α-CH_2 group is prochiral since the two protons are not made magnetically equivalent by rotation. However the ^1H NMR spectrum does not show clear evidence of this, although the triplet (J = 1.3 Hz) splitting implying equal coupling to both γ-protons is perhaps anomalous,[8] and may in reality be a poorly resolved AB spectrum with a very small value of δ_{AB}.

Dry hydrogen chloride cleaves the allyl group from silicon to yield the chlorosilacyclopentanes whose configurations are known.[2] Table III contains the results of several experiments on allyl derivative mixtures with similar *E,Z/Z,E*:*E,E* ratios but differing *Z,Z* contents. There appears to be a slightly greater reactivity for the *E,Z/Z,E* isomer than the other isomers (mainly *E,E*) as judged by experiments 2 and 5, but most obviously the reaction is stereospecific with *inversion at silicon*. This is not a consequence of isomerization of the chloro compounds since we have shown[2] that although the equilibrium favors the *Z,Z* isomers the equilibrium constant is only 1.2 (±0.1)

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Table IV. $HgCl_2$ Cleavage of 1-Allyl-1,2,5-trimethyl-1-silacyclopentane

expt no.	composition of initial allyl[a]			composition of unreacted allyl[b]			composition of chloro product[b]		
	E,Z/Z,E	*Z,Z*	*E,E*	*E,Z/Z,E*	*Z,Z*	*E,E*	*E,Z/Z,E*	*Z,Z*	*E,E*
1	46	33	21	63[c]		37	68.5	23	8.5
2	64[c]		36	52.5[c]		47.5	55	28.5	17

[a] By GC (and ^1H NMR expt no. 1). [b] By GC. [c] *E,Z/Z,E* + *Z,Z*.

corresponding to *Z,Z*:*E,E* ≃ 55:45.

This is the result expected for S_N2 attack by chloride on silicon in the ion pair formed by protonation of the allyl group at the γ-carbon. It should indeed be the *E,E* isomer, as our results suggest; it is the least reactive, but only if this step is rate controlling. However, the five-membered ring would be required to span two equatorial positions in this transition state, and such configurations are considered to be unfavorable. It may be that the alternatives, which necessarily place either entering or leaving groups equatorial, present greater problems.

Sommer, Tyler, and Whitmore[6] report that HCl under reflux converts allyltrimethylsilane to chlorotrimethylsilane and propane, but that in the cold HBr yields (2-bromo-1-propyl)trimethylsilane which is converted to propene and bromotrimethylsilane on heating. These results imply that addition of acid and the loss of the allyl group are distinct steps with the latter slower.

Mercuric chloride cleavage proceeds much more slowly, at least partially because the system is heterogeneous, and the products of incomplete reaction were obtained. Our results are summerized in Table IV. It is clear that the *E,E*-allyl isomer is less reactive than the *E,Z/Z,E* (and/or the *Z,Z*) since the unreacted material is enriched. Furthermore the chloro product is deficient in the *E,E* isomer so that the reaction has proceeded with *retention of configuration at silicon*. Detailed analysis of the data is consistent with complete retention of configuration (based on the initial assumption that *E,Z/Z,E*-allyl yields *E,Z/Z,E*-chloro) and the data are inexplicable if substantial inversion takes place. On this basis relative reactivities can be deduced from the logarithms of the extent of reaction giving *E,Z/Z,E*:*Z,Z*:*E,E*-allyl reactivities = 1.45:1.2:1 from experiment 1 and, for experiment 2, (*E,Z/Z,E* + *Z,Z*):*E,E* = 1.35:1 which is essentially the weighted mean value.

Retention of configuration at Si is suggestive of a six-membered cyclic transition state with allylic rearrangement. From a study of models, which show that minor distortions may have a considerable effect, it is not obvious to us what relative reactivities are to be expected for the three geometrical isomers. Confirmation that allylic rearrangement does indeed take place is required. Unfortunately a confusing mixture of products and reactants is obtained from the methallyl derivative.[9] Clearly considerable further work needs to be done on this reaction, and the 1,2-dimethyl-1-silacyclopentane system from which we can obtain the *cis*-crotyl derivative may prove more amenable.[10]

Roberts[12] has reported rate studies, which are complex, on the reaction of allyltrimethylsilane with mercuric chloride in acetonitrile to yield allylmercuric chloride. Also reported[13] are the corresponding reactions of allyl and crotyltriethylgermane. In the latter case the product is crotylmercuric chloride, but it was suggested that this, the thermodynamically favored product, arose by rapid rearrangement of the initially formed methallylmercuric chloride.

Table V. ^{13}C Chemical Shifts of 1-(Trifluoroacetoxy)-1,2,5-trimethyl-1-silacyclopentane[a]

	E,Z/Z,E	*E,E*	*Z,Z*
Si-CH_3	−5.89	−7.92	−3.35
C-CH_3	14.24, 13.27	14.33	13.78
C_2,C_5	21.45, 20.34	18.79	20.08
C_3,C_4	33.92, 33.88	32.73	32.80

[a] In ppm relative to internal Me_4Si.

Analysis of the reaction mixture obtained from the action of bromine on the allyl derivative proved to be quite difficult. The only products that could be identified with certainty, because they show NMR resonances at characteristic chemical shifts, were at least two (2,3-dibromopropyl)-1,2,5-trimethyl-1-silacyclopentanes. Thus, the ^1H NMR spectrum shows multiplets at δ 4.2 ($CH_2CHBrCH_2Br$) and δ 3.6–3.8 (CH_2Br), and the ^{13}C NMR spectrum has resonances at 50.5, 50.2 (*C*HBr) and 40.5, 40.4 (CH_2Br). Sommers, Tyler and Whitmore[6] did not obtain an addition product by the action of bromine on allyltrimethylsilane. However with chlorine the formation of (2,3-dichloro-1-propyl)trimethylsilane was observed.

Trifluoroacetolysis of the allyl derivative in $CDCl_3$ solution proceeds quite readily at room temperature to yield propene, identified by its ^{13}C NMR spectrum (133.9, 115.6, and 18.8 ppm) and the ^2H NMR spectrum (δ 1.8) of CH_2=$CHCH_2D$ obtained when CF_3CO_2D is employed. But, unlike the reactions with HCl and with $HgCl_2$, the reaction does not appear to be stereospecific at silicon. Thus allyl derivative having *E,Z/Z,E*:*E,E* = 64:36 and free of *Z,Z* isomer (^{13}C NMR) yielded trifluoroacetoxy derivatives having *E,Z/Z,E*:*E,E*:*Z,Z* = 63:17:21, while other mixed allyl isomers gave nonstereospecific product mixtures with *E,E* > *Z,Z*. On the other hand, a sample of *E,Z/Z,E* allyl derivative containing a little *E,E* isomer gave *E,Z/Z,E*-trifluoroacetate containing only its *Z,Z* isomer. The cleavage reaction may well be stereospecific, but the products may suffer equilibration by excess trifluoroacetic acid to varying extents in the various experiments. We are investigating this matter further in a more general study of the trifluoroacetolysis of allylic silanes.

We had previously mentioned[2] the trifluoroacetoxy derivatives arising from the action of trifloroacetic acid on the acetoxy derivatives of the 1,2,5-trimethyl-1-silacyclopentanes. (It was considered that the reactions proceeded with inversion at silicon and there was no evidence of equilibration of *E,E* and *Z,Z* isomers). Authenticated NMR data for the trifluoroacetates being essential for the present studies, these were prepared by two methods and their ^{13}C NMR characteristics are listed in Table V. In addition to the resonances listed each compound also

(9) Prepared as for the allyl derivative but employing the Grignard reagent from either 3-chloro-1-butene or 1-chloro-2-butene, a mixture of isomers including two diastereomers of the *E,Z/Z,E* derivative is obtained.

(10) By $Cr(CO)_6$ induced photoreaction of the purified *E*- and *Z*-isomers of the silane with butadiene; cf. the corresponding reaction of trimethylsilane.[11]

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shows CF_3 (116.2, q, J (C–F) = 285.5 Hz) and $C{=}O$ (161.4, q, J (C–F) = 44 Hz). The Si–CH_3 resonances in the ^1H NMR spectrum at 0.44, 0.42, and 0.52 ppm for the $E,Z/Z,E$, and E,E, and the Z,Z isomer, respectively, were also used for analytical purposes.

Experimental Section

Proton NMR spectra were determined on JEOL JNM-MH-100 and JEOL JNM-PS-100 instruments (100 MHz) and at the National NMR Center, Canberra, Australia (270 MHz); ^{13}C NMR spectra were determined on a JEOL JNM-FX-100 instrument (25 MHz **and** at the National NMR Center (68 MHz); ^2H NMR spectra were obtained at 15.29 MHz on the JEOLJNM-FX-100. All spectra were run in CDCl solutions with Me_4Si or $CHCl_3$ as internal standard. Gas chromatographs were obtained by using a Varian Aerograph 200 GC instrument with a SGE GSB/SE30/S SGOT glass capillary column (minimum effective plate number of 20 000). Mass spectra were recorded at 70 eV on an MS902S spectrometer.

1-Allyl-1,2,5-trimethyl-1-silacyclopentane. The Grignard reagent, prepared magnesium (0.96 g, 40 mM) and allyl bromide (4.8 g, 40 mM) in dry ether (50 mL), was reacted with 1-chloro-1,2,5-trimethyl-1-silacyclopentane (1.6 g, 10 mM) of isomeric composition $E,E:E,Z/Z,E:Z,Z$ = 31:47:23, followed by hexane (50 mL). Most of the ether was removed by distillation and the reaction mixture was refluxed on a hot water bath for ~24 h. The filtered reaction mixture was reduced in volume, hydrolyzed with water, extracted into ether, and distilled to yield a crude product (1.3 g) (ca. 30% yield with allowance for the hexane present), bp ~115 °C (80 mm), which contains some residual hexane. The mass spectrum of the crude product showed the following peaks: m/e (relative intensity) 168 (11), 127 (51), 126 (24), 99 (100), 85 (56), 59 (53), 57 (40), 56 (53), 43 (36). NMR spectroscopy and GC analysis showed the product to be composed of two isomers of the title compound $E,E:E,Z/Z,E$ = 47:53 with the ~40% hexane. The retention times for the $E,Z/Z,E$ and E,E isomers on analytical GC were 15.2 and 15.8 min respectively at 80 °C. Careful distillation under reduced pressure gave product free of hexane, bp ~100 °C (60 mm), with the isomers in the ratio $E,E:E,Z/Z,E$ = 31:69 perhaps containing a small amount of the Z,Z isomer.

Reactions of 1-Allyl-1,2,5-trimethyl-1-silacyclopentane. With Hydrogen Chloride. The allyl derivative (ca. 0.05 g) in dry ether solution, (ca. 5 mL) was treated with excess HCl dissolved in dry ether (ca. 5 mL) for ca. 5 min at room temperature after which the ether and excess HCl were removed by cold rotary evaporation and the product examined by gas chromatography as described in ref 2.

With Mercuric Chloride. The allyl derivative (ca. 0.1 g) in dry ether solution (ca. 10 mL) was treated with 1 equiv of $HgCl_2$ (ca. 0.15 g) and the suspension was refluxed for ca. 12 h. Hexane was added, most of the ether removed by evaporation, and then filtration followed by evaporation yielded the product which was examined by gas chromatography and by NMR spectroscopy. Metallic mercury, and probably also Hg_2Cl_2, were produced during the reaction and were removed during workup. No allyl mercurials were detected after workup but these may well not survive.

With Bromine. The allyl derivative (ca. 0.1 g) in carbon tetrachloride solution (ca. 20 mL) was treated with a solution of bromine in carbon tetrachloride until the bromide color persisted. A complex reaction product was obtained from which by careful distillation material containing 1-(2,3-dibromopropyl)-1,2,5-trimethyl-1-silacyclopentane, identified by ^1H and ^{13}C NMR spectroscopy, was obtained. The product also contains bromosilanes which seem to be formed by decomposition of the dibromopropyl derivative during attempts at purification.

With Trifluoroacetic Acid. The allyl derivative (0.16 g, 1 mM) in $CDCl_3$ (2 mL) was treated with trifluoroacetic acid (ca. 0.3 g, 3 mM) and after 3 h, the ^{13}C NMR spectrum was recorded. Further, acid was added and after several hours ^1H, ^2H, and ^{13}C NMR spectra were employed to analyze the reaction product.

1-(Trifluoroacetoxy)-1,2,5-trimethyl-1-silacyclopentane. Method A. 1-Chloro-1,2,5-trimethyl-1-silacyclopentane (0.18 g, 1.1 mM) of isomeric composition $E,Z/Z,E:E,E:Z,Z$ = 46:47:7 in CDL_3 (3.46 g) was shaken with silver trifluoroacetate (0.36 g, 1.7 mM) for 12 h. After filtration the solution was examined by ^1H and ^{13}C NMR spectroscopy and found to contain the trifluoroacetates with composition $E,Z/Z,E:E,E:Z,Z$ = 47:35:18.

Method B. 1,2,5-Trimethyl-1-silacyclopentane (0.15 g, 1.2 mM) of isomeric composition $E,Z/Z,E:E,E$ = 41:59 in $CDCl_3$ (3.28 g) was shaken with mercuric trifluoroacetate (0.58 g, 1.5 mM) for 12 h. The solution was decanted and filtered before examination by ^1H and ^{13}C NMR spectroscopy. The product contained unreacted hydride with $E,Z/Z,E:E,E$ = 48:52 and trifluoroacetates with $E,Z/Z,E:E,E:Z,Z$ = 37:46.5:16.5.

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Registry No. Allyl bromide, 106-95-6; (*E,E*)-1-chloro-1,2,5-trimethyl-1-silacyclopentane, 71518-76-8; (*E,Z*)-1-chloro-1,2,5-trimethyl-1-silacyclopentane, 71564-07-3; (*Z,Z*)-1-chloro-1,2,5-trimethyl-1-silacyclopentane, 71564-08-4; (*E,E*)-1-allyl-1,2,5-trimethyl-1-silacyclopentane, 88916-34-1; (*E,Z*)-1-allyl-1,2,5-trimethyl-1-silacyclopentane, 88979-74-2; (*Z,Z*)-1-allyl-1,2,5,-trimethyl-1-silacyclopentane, 88979-75-3; (*E,E*)-1-(trifluoroacetoxy)-1,2,5-trimethyl-1-silacyclopentane, 88979-76-4; (*E,Z*)-1-(trifluoroacetoxy)-1,2,5-trimethyl-1-silacyclopentane, 88916-36-3; (*Z,Z*)-1-(trifluoroacetoxy)-1,2,5-trimethyl-1-silacyclopentane, 88979-77-5; 1-(2,3-dibromopropyl)-1,2,5-trimethyl-1-silacyclopentane, 88916-35-2; hydrogen chloride, 7647-01-0; mercuric chloride, 7487-94-7; bromine, 7726-95-6; trifluoroacetic acid, 76-05-1.

Heterocyclic Studies. 48. Multiple Rearrangments of a 9-Methyl-1,9-diazabicyclo[4.2.1]nonadienone[1]

James A. Moore,* Otis S. Rothenberger,[2] William C. Fultz, and Arnold L. Rheingold

Department of Chemistry, University of Delaware, Newark, Delaware 19711, and Illinois State University, Normal, Illinois

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The pyrazolopyran **5** is obtained by thermal rearrangement of the diazabicyclooctadienone **3**; a concerted [3.3] sigmatropic process is suggested. Treatment of **3** with sodium methoxide in methanol leads to the tetrahydropyridazine **14** and the tetrahydroindazolone **16** via the acyclic carbanion **13**. Photoisomerization of **3** gives the caged ketone **18**.

The diaz. dienones **1** and **3**, available by 1,3-dipolar cycloaddition of dimethyl acetylenedicarboxylate to diazepinium azomethine imines[3] contain an unusual array of functional groups and present the possibility of rather

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