Table I NMR Data for Ferrelactones[a]

Compound	Position	Chemical shifts (ppm)	Coupling constants (Hz)
5	1	1.34	$J_{1,2} = 6.5$
	2	4.39	$J_{2,3} = 4.0$
	3	4.58	$J_{3,4}$ = undetermined
	4	4.63	$J_{4,5} = 12.0$
	5	4.14	$J_{5,6} = 6.0$
	6	1.88	
6	1	1.43	$J_{1,2} = 6.5$
	2	4.60	$J_{2,3} = 5.2$
	3	5.13	$J_{3,4} = 8.7$
	4	4.31	$J_{4,5} = 9.7$
	5	4.81	$J_{5,6} = 7.4$
	6	1.80	
7	1	1.32	$J_{1,2} = 6.5$
	2	4.25	$J_{2,3} = 1.2$
	3	4.38	$J_{3,4} = 7.5$
	4	4.77	$J_{4,5} = 12.0$
	5	4.03	$J_{5,6} = 6.0$
	6	1.84	

[a] NMR spectra were obtained using a Varian HA-100 or HR 220 with TMS as internal standard at δ 0.00 ppm and $CDCl_3$ as solvent.

compared to 1.2 Hz for trans $^3J_{2,3}$ in **7** suggesting a cis arrangement for these protons in **5**. Similarly $^3J_{2,3}$ of 5.2 Hz in **6** indicates a cis relationship. Considering the C_4 and C_5 protons, values of 12.0 Hz in **7** and **5** fix these as trans while a value of 9.75 Hz indicates a cis orientation in **6**. Further evidence for the relative stereochemistry at C_4 and C_5 in **5**, **6**, and **7** was obtained by observing induced chemical shifts using $Eu(fod)_3$. The induced downfield shifts for the C_5 proton in **5**, **6**, and **7** were 10.0, 9.9, and 3.8 ppm per mole of $Eu(fod)_3$ per mole of ferrelactone, respectively. The downfield shifts for the C_5-methyl group in **7**, **5**, and **6** were 2.1, 2.1, and 5.8 ppm per mole of $Eu(fod)_3$ per mole of ferrelactone, respectively. Assuming a model in which the shift reagent is coordinated with the lactone ring, the relative large shift of the C_5 methyl group and relatively small shift of the C_5 proton in **6** indicates a cis stereochemistry. Since **7** is known to be trans (X-ray), similarity in its shift behavior with **5** indicates a trans stereochemistry for the latter.

With the structures of ferrelactones **5**, **6**, and **7** established, the stereochemical results may be summarized as follows: **1** → **5** proceeds with *retention* of configuration about the C_4–C_5 double bond, but a *change* in the relative configuration between C_2 relative to C_3. This change amounts to rotation about the C_2–C_3 bond. Reaction **2** → **6** proceeds with overall *retention* of the stereochemical relationships between reactant and product.

In the sequence of reaction steps leading to the ferrelactone the generation of the allylic system is of key importance. A priori this could occur in two distinct ways, namely, initial complexation of the double bond with photochemically generated $Fe(CO)_4$ followed by cleavage of the oxido ring and lactone formation, or, alternatively, initial complexation of the oxido oxygen with the electrophilic $Fe(CO)_4$ and ring cleavage followed by lactone formation. Since neither route uniquely accounts for the observed stereochemical course, the mechanistic aspects of this reaction remain a continuing research objective.

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(3) Epoxidation[4] of *trans,trans*-2,4-hexadiene (CH_3CO_3H, CH_2Cl_2, 0°) yielded **1** in 89% yield: bp 21–22 (0.05 mm); NMR δ H_1 1.29, H_2 2.86, H_3 3.00, H_4 5.91, and H_6 1.70; J (Hz) $J_{1,2}$ 5.2, $J_{2,3}$ 2.2, $J_{3,4}$ 8.1, $J_{3,5}$ 0.4, $J_{4,5}$ 15.6, $J_{4,6}$ 1.6, and $J_{5,6}$ 6.6. *cis,cis*-2,4-Hexadiene yielded **2**: bp 20–21 (0.08 mm); NMR δ H_1 1.25, H_2 3.19, H_3 3.62, H_4 5.22, H_5 5.85, and H_6 1.78; J (Hz) $J_{1,2}$ 5.5, $J_{2,3}$ 4.4, $J_{3,4}$ 8.1, $J_{3,5}$ 1.0, $J_{4,5}$ 11.1, $J_{4,6}$ 1.7, and $J_{5,6}$ 7.1. *cis,trans*-2,4-Hexadiene yielded **3** and **4**, and they were not separable by fractional distillation.

(4) J. K. Crandall and L. H. Chang, *J. Org. Chem.*, **32**, 532 (1967).

(5) The thermal reaction will be reported in the full paper. It was found that **1** with $Fe_2(CO)_9$ in ether (36°, 2 hr) yielded 7 and **5** in 1:6 ratio in 83% yield. Under the same conditions **2** yielded 7 and **6** in 5:1 ratio in 51% yield.

(6) Irradiations were carried out in an *all* quartz system. Compound **5** had mp 130–131°. Anal. Calcd for $C_{10}H_{10}O_5Fe$: C, 45.11; H, 3.79. Found: C, 45.22; H, 3.90. Acyl carbonyl 1672 cm^{-1}; C≡O, 1990, 2004, and 2034 cm^{-1}. Compound **6** had mp 103–104. Anal. Calcd for $C_{10}H_{10}O_5Fe$: C, 45.11; H, 3.79. Found: C, 44.99; H, 3.86. Acyl carbonyl, 1674; C≡O, 1999, 2008, and 2040 cm^{-1}. Compound 7 had mp 108–109°. Anal. for $C_{10}H_{10}O_5Fe$: C, 45.11; H, 3.79. Found: C, 45.00; H, 3.89. Acyl carbonyl, 1670 cm^{-1}; C≡O, 1995, 2005, and 2035 cm^{-1}. The starting 2,3-oxidohex-4-enes were stable under the photolytic conditions in the absence of $Fe(CO)_5$.

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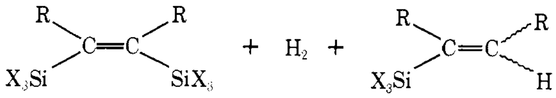
A Novel Dehydrogenative Cis Double Silylation of Internal Acetylenes with Hydrosilanes. Catalysis by Diethyl(bipyridyl)nickel(II)

Sir:

There have been two types of addition reactions of silicon hydrides to carbon-carbon multiple bonds in the presence of transition metal catalysts. One is the well-known hydrosilylation[1] and the other the recently discovered, nickel or palladium catalyzed, double silylation of dienes and acetylenes with disilicon hydrides involving the cleavage of the Si-Si bond while leaving intact the Si-H bond.[2] We report here the third type of addition reaction, viz., dehydrogenative, stereoselective cis double silylation of internal acetylenes with monosilicon hydrides catalyzed by diethyl(bipyridyl)nickel(II), as represented by eq 1.

$RC{\equiv}CR + HSiX_3 \longrightarrow$



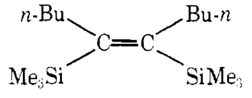
(1)

Table I. Reaction of $HSiX_3$ with Acetylenes in the Presence of $[Ni(bpy)Et_2]$ as a Catalyst in Ether at Room Temperature[a]

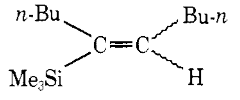
$HSiX_3$	Acetylene	Time[b] (hr)	Products[c] (yield %)[d] I[e]	II (E:Z)
$HSiCl_3$	$EtC\equiv CEt$	4	62[f,g]	7[h]
$HSiCl_3$	n-$BuC\equiv CBu$-n	2	77[i]	13 (39:61)
$HSiCl_3$	n-$BuC\equiv CBu$-n[j]	4	74	17 (57:43)
$HSiCl_3$	n-$BuC\equiv CSiMe_3$	20	k	—
$HSiCl_2Me$	$EtC\equiv CEt$	70	56[l]	11[h]
$HSiCl_2Me$	n-$BuC\equiv CBu$-n	14	72	24 (73:27)
$HSiCl_2Me$	n-$BuC\equiv CBu$-n[m]	64	69	22 (79:21)
$HSiCl_2Me$	$PhC\equiv CMe$	49	27	52[n]
$HSiCl_2Me$	$PhC\equiv CPh$	24	3[o]	60 (81:19)

[a] Unless otherwise noted, $HSiX_3$:acetylene:catalyst $\simeq$10:1:0.1; bpy = bipyridyl. [b] The approximate duration of the blue-black or green color of the reaction mixture (see text). [c] I refers to the double silylation product and II the hydrosilylation product; cf. Scheme I. [d] Determined by quantitative GLPC after methylation, based on the acetylenes. [e] *Z*-Isomer, unless otherwise noted. [f] *E*:*Z* = 11:89. [g] $Et(Me_3Si)C{=}C(SiMe_2H)Et$, 3.5%. [h] Appeared as an inseparable broad peak on GLPC. [i] n-$Bu(Me_3Si)C{=}C(SiMe_2H)Bu$-$n$, 4%. [j] $HSiCl_3:BuC\equiv CBu$:catalyst $\simeq$ 2.8:1:0.1. [k] Several uncharacterized products, along with 82% unchanged acetylene. [l] $Et(Me_3Si)C{=}C(SiMe_2H)Et$, 8.5%. [m] $HSiCl_2Me:BuC\equiv CBu$: catalyst $\simeq$ 5.3:1:0.1. [n] Consisting of four possible (*E, Z*, α, β) isomers. [o] Only *E* isomer was formed, cf. ref 7.

Thus, to a deep green solution of diethyl(bipyridyl)nickel(II)[3] (0.54 mmol) in ether (20 ml) was added trichlorosilane[4] (54 mmol) in one portion at room temperature under nitrogen. The mixture immediately deposited brown precipitate. After 20 min of stirring 5-decyne (5.4 mmol) was added. Immediately, a blue-black mixture resulted and a rapid evolution of hydrogen set in. After about 2 hr the color changed back to brown and the evolution of hydrogen ceased, clearly indicating the completion of the reaction. GLPC analysis after treatment with methylmagnesium bromide[5] showed the formation of (*Z*)-5,6-bis(trimethylsilyl)-5-decene (**1**)[6,7] in 77% yield based on the 5-decyne, in addition to the normal hydrosilylation products, 5-trimethylsilyl-5-decene (**2**), in 13% yield (*E*:*Z* = 39:61).[8] The hydrogen evolved was almost equivalent (>90%) to the double silylation product. The unequivocal assignment of the *Z* configuration for the double silylation product **1** was made as follows. Firstly, upon heating at 250-300° for 4 hr in a sealed tube,[9] the *liquid* product **1**, bp 112-113° (7 mm), was converted quantitatively to the other *crystalline* isomer **1′**, mp 46-47°,[6] which had the shorter retention time on GLPC than the former, but had superimposable NMR and ir spectra.[10] Secondly, the stereochemical course of desilylation of both the isomers by the action of an excess of sodium ethoxide in DMSO (130°, 15 min)[9,11] was as follows: **1′** gave (*Z*)-**2** (6%) and (*E*)-5-decene (90%) along with unchanged **1′** (4%), while from **1** were obtained (*E*)-**2** (53%) and 5-decene (47%, *E*:*Z* $\simeq$ 40:60). The quantitative total yields of the desilylation products and the former three stereospecific transformations give positive proof of the *Z* configuration for the direct reaction product **1**, and in turn the cis double silylation.



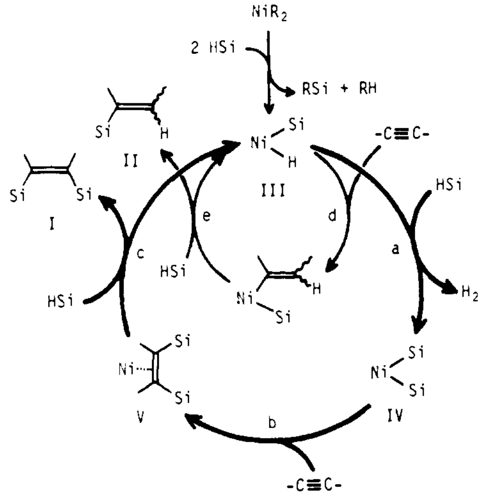
1



2

Results summarized in Table I reveal several notable trends. The "unactivated" dialkylacetylenes[12] show a great preference for the double silylation as shown by the order n-$BuC\equiv CBu$-n > $EtC\equiv CEt$ > $PhC\equiv CMe$ ≫ $PhC\equiv CPh$, while the hydrosilylation increases in the reverse order.[13] The low reactivity of $Me_3SiC\equiv CBu$-n may be due to steric reasons.[15] $HSiCl_3$ is much more reactive and shows a slightly greater preference for the double silylation than $HSiCl_2Me$.[16] The silane-to-acetylene ratios have little effect on the extent of the double silylation but a great effect on the reaction rates.

Scheme I[a]



[a] Bipyridyl ligand on nickel and substituents on silicon and on acetylene are omitted for clarity.

Scheme I illustrates the catalytic cycle for the novel dehydrogenative double silylation, together with the hydrosilylation.[18] A (hydrido)(silyl)nickel complex (III) is regarded as a key intermediate for the catalysis. Successive attacks on it by a "reactive" hydrosilane (step a), an "unactivated" acetylene (step b), and again by another molecule of hydrosilane (step c) lead to the double silylation product (I), while the reverse order of attacks by an "activated" acetylene (step d) and a "less reactive" hydrosilane (step e) gives rise to the normal hydrosilylation product (II) predominantly. The bipyridyl ligand may be indispensable to the stabilization of the silyl-nickel intermediates. Our recent isolation studies of the disilylnickel (IV)[17] and the disilylolefin-nickel complex[7] analogous to V justify the proposed catalytic cycle. The competitive nature of the present catalytic reactions implies the comparable affinities of acetylene and hydrosilane for the nickel complexes.

The novel double silylation is also of synthetic value. This offers the first stereoselective route to disilylolefins from "unactivated" dialkylacetylenes and readily available hydrosilanes, while double silylations of "activated" acetylenes have recently been reported.[2,19,20]

Investigations are continuing into the extention of this novel reaction to other unsaturated compounds and synthetic utility of the disilylolefins thus obtained.

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(4) The ether was distilled from $LiAlH_4$ and the chlorosilanes from quinoline under nitrogen just before use.

(5) The products containing polychlorosilyl groups showed decomposition peaks on the GLPC column.

(6) Satisfactory elemental analyses and consistent NMR and ir spectral data were obtained for all the products reported here.

(7) The NMR and ir spectral data were reported previously: Y. Kiso, K. Tamao, and M. Kumada, *J. Organomet. Chem.*, **76**, 105 (1974).

(8) A small amount (∼4% yield) of [possibly (*Z*)]-*n*-Bu(Me_3Si)C═C(SiMe_2H)Bu-*n* was also formed owing to the concomitant H–Cl interchange on the silicon atom characteristic of the interaction of hydrochlorosilanes with nickel complexes; Y. Kiso, M. Kumada, K. Tamao, and M. Umeno, *J. Organomet. Chem.*, **50**, 297 (1973); Y. Kiso, M. Kumada, K. Maeda, K. Sumitani, and K. Tamao, *ibid.*, **50**, 311 (1973).

(9) The present thermal isomerization and alkali–desilylation are based on the recent observations by Dr. H. Okinoshima; dissertation submitted to Kyoto University, 1975. We thank him for valuable suggestions.

(10) The empirical melting point rule strongly suggests the *Z* configuration for the liquid isomer: E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, pp 326–327.

(11) Cf. C. C. Price and J. R. Sowa, *J. Org. Chem.*, **32**, 4126 (1967).

(12) Cf. J. A. Labinger, J. Schwartz, and J. M. Townsend, *J. Am. Chem. Soc.*, **96**, 4009 (1974).

(13) Hydrosilylation of internal acetylenes under such mild conditions as presently employed is also noteworthy.[14]

(14) M. F. Lappert, T. A. Nile, and S. Takahashi, *J. Organomet. Chem.*, **72**, 425 (1974).

(15) Although *n*-BuC≡CH readily reacted with $HSiCl_2Me$ under similar conditions, a mixture of several products was formed. None of them has yet been characterized, but see ref 14.

(16) The reaction of $HSiClMe_2$ with 5-decyne (∼100 hr) gave 50–80% yield of 5-decene ($Z{:}E \simeq 80{:}20$) instead of the double silylation product, together with 50–20% yield of the hydrosilylation product. It has previously been recognized that silanes containing no chlorine atoms do not exhibit reactivity.[17]

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Solid Phase Organometallic Synthesis. Bis(di-*n*-butylchlorotin)tetracarbonylosmium

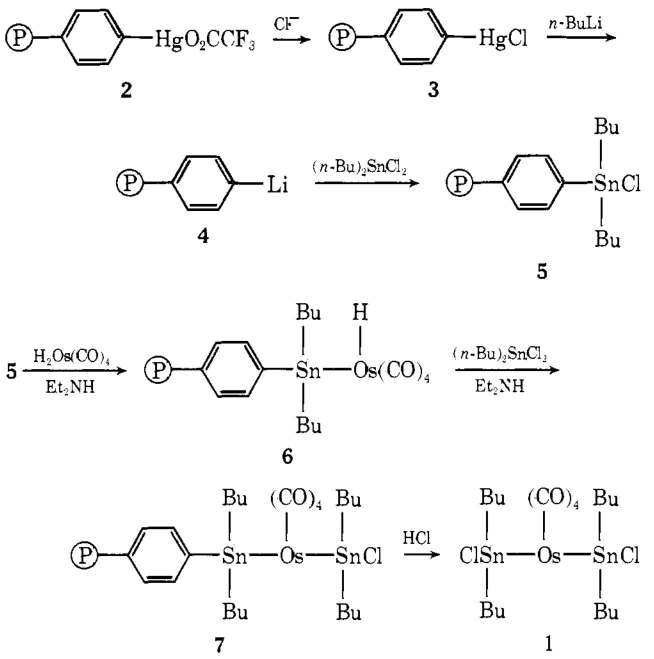
Sir:

Herein we describe the solid phase synthesis and subsequent isolation of the title compound, **1**, from di-*n*-butyltin dichloride and dihydridotetracarbonylosmium with diethylamine as the coupling agent (see Scheme I). Polymer attachment circumvented formation of bis(μ-dibutyltin-tetracarbonylosmium), the cyclic product from the known reaction of these components in solution.[1]

Since Merrifield's discovery of the solid phase method for peptide synthesis,[2] several useful applications have been found for polymer-bound reagents[3] and catalysts.[4] Repetitive, sequential-type syntheses using insoluble polymer supports have been described for peptides,[2] oligonucleotides,[5] and oligosaccharides.[6]

Multiple step syntheses with unprotected multifunctional reactants are much less common.[3b] Polymer "immobilized" ester enolates have been monoacylated[7] and several reactions of terephthalaldehyde have been described[8a] including its stepwise conversion to 4,4′-stilbenedicarbaldehyde.[8b] For these applications, relatively low levels of substitution limited reaction of one polymer-bound moiety with another.[7,8] In contrast, apparent chelate properties of phosphine-substituted copolymers have been attributed to polymer chain mobility.[9] While present information is inadequate to reconcile these seemingly contradictory observations, it is clear that intrapolymer reactions pose a significant threat to the success of any solid phase synthesis scheme that utilizes unprotected, multifunctional components.

Scheme I



The choice of a macroreticular styrene–20% divinylbenzene copolymer for this work was based upon observations by Grubbs and coworkers[10] that the higher degree of cross-linking in this porous polymer permits much less internal mobility than in the 2% cross-linked gels commonly used for peptide synthesis[11] and catalyst support.[9] Other important considerations were the requirements that the distance between substituents on the resin must be chosen to minimize intrapolymer reactions and the pores must be large enough to permit growth and removal of the product molecules.[12] The phenyl–tin bond served as the cleavable connecting link. To ensure its exclusive formation, aromatic mercuration[13] was selected for the initial functionalization.[14] Unpolymerized vinyl groups on the polymer were deactivated toward mercuration[16] by treatment with *n*-butyllithium (TMEDA complex)[17] followed by methanolysis. The dried resin was stirred in a dilute solution of $Hg(O_2CCF_3)_2$[18] at 0° for 18 hr and the resino-phenylmercuric trifluoroacetate[19] **2** was converted to the corresponding chloride **3** with excess tetramethylammonium chloride in methanol. Microscopic examination of a bisected bead from a portion of **3**, that had been reduced with lithium naphthalenide[21] in THF and quenched in methanol, revealed fairly even distribution of elemental mercury.[24]

Treatment of **3**[25] under argon with 0.75 *M* *n*-BuLi in toluene (1.5 mequiv/g) for 1 hr followed by exhaustive washing with toluene and ether gave resino-phenyllithium, **4**. This was quenched with excess $(n\text{-Bu})_2SnCl_2$ (2.0 mmol/g) in ether.[26] The first metal-to-metal bond was formed when **5** (8.0 g having 0.022 mequiv of Cl/g) was stirred with a solution of $H_2Os(CO)_4$ (0.65 mmol) and diethylamine (1 ml) in 1:1.5 THF-CH_2Cl_2 for 2.5 hr under argon. The infrared spectrum of the washed and dried resin **6** (1% in KBr)[27] exhibited ν_{CO} at 2113 m, 2048 m, and 2026 vs cm^{-1}, similar to the spectrum of *cis*-$Ph_3SnOs(CO)_4H$;[1] a weak absorption at 1937 cm^{-1} is tentatively assigned to ν(Os–H). Treatment of **6** with $(n\text{-Bu})_2SnCl_2$ (3.28 mmol) in CH_2Cl_2 (10 ml) containing Et_2NH (1 ml) as above gave the resino-trimetalide **7**[28] with an infrared spectrum (ν_{CO} 2048 vw and