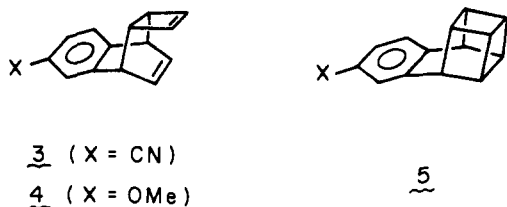


Figure 2. Correlations between the vacant orbitals of ethylene, substituted benzenes, and substituted benzene-ethylene complexes used as models for benzonorbornadienes.

has been reported: 2-cyanobenzobarrelene gives a triplet di- π -methane arrangement product resulting from exclusive benzo-vinyl (C-3) bridging.⁴ The case of donor substitution is predicted to give similar regioselectivity, now due to HOMO coefficient differences.

That such an apparently naive model captures the essential origin of the observed regioselectivity has been verified by semiempirical CNDO/S-CI calculations⁵ on the excited states of various model systems. In benzene and monosubstituted benzenes, the lowest triplet states (3L_a or $^3B_{1u}$) are composed of an equal mixture of configurations resulting from a_2 to a_2 promotion and b_1 to b_1 promotion. The introduction of methyls at C-3 and C-4 reduces the molecular symmetry to C_s , perturbing this simple picture. Bringing an ethylene group into the proximity of C-3 and C-4 in a parallel plane further reduces the symmetry of the system, and calculations on the full benzonorbornadiene introduce the additional complication of σ - π mixing. As a result, calculations on benzonorbornadiene give orbitals of unrecognizable shapes, and the triplet state is a complex mixture of configurations. For that reason, we use the substituted *o*-xylene-ethylene complex as an easily understood, yet sufficiently high-order, approximation to the full molecule. Figure 2 shows the relevant vacant orbitals of ethylene, two substituted *o*-xylenes, and of the complexes, where the component molecules are separated by 2.5 Å.⁶ The LUMO of the complex may be considered to result from mixing the ethylene LUMO in a bonding fashion with both of the two low-lying orbitals of the aromatic moiety. In the methoxy-substituted aromatic, both of the aromatic orbitals contribute to nearly the same extent, but the resulting LUMO meta and para coefficient magnitudes are dominated by the aromatic LUMO. The cyano-aromatic LUMO mixes most with the ethylene LUMO and dominates the resulting meta and para coefficient magnitudes. Although the situation is more complicated than suggested by the model proposed at the outset of this paper, the simple model contains in it the essential reason for regioselectivity.

Finally, we turn to another aspect of selectivity noted by Paquette and co-workers.¹ In the benzo-tricyclic systems, **3** and **4**, the direction of preferential di- π -methane bridging is identical with that observed for **1** and **2**; that is, **3** gives a di- π -methane product resulting from para bridging, **4** from meta



bridging. However **4** also gives the intramolecular [2 + 2] cycloaddition product, **5**.¹ The kernel of an explanation for these phenomena is contained in Figure 2. Whereas the low-lying nature of the acceptor-substituted aromatic vacant orbitals leads to an excited state more localized on the aromatic moiety, and this leads to aryl-vinyl bridging, donor substituents cause the lowest triplet to be more ethylene $\pi\pi^*$ in nature, increasing the propensity for bridging of ethylene to a second ethylene moiety.

Calculations which validate the last rationale, rationalizations of specificity in ortho-substituted benzonorbornadienes, and extensions of these ideas to photochemical substituent effects in general will be reported in due course.⁷

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- (6) Since CNDO/S considers a σ interaction to be 1.71 times stronger than a π interaction for the same overlap, this corresponds, in reality, to a very close approach of ethylene to the aromatic ring. Calculations performed at greater distances give the same results as those reported here, but the amount of mixing is decreased.
- (7) Zimmerman's explanation for the relative facility of benzo-vinyl, vinyl-vinyl, and α - or β -naphtho-vinyl bridging, based on the triplet energies of hydrocarbons isocorjugate with the "transition state" for bridging,² is, we believe, equivalent to the orbital model we propose here.
- (8) Camille and Henry Dreyfus Teacher-Scholar Grant Recipient, 1972-1977; Alfred P. Sloan Foundation Fellow, 1975-1977.

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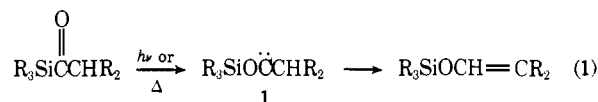
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Silicon-Carbon Double Bonds: New Route, New Substituents, New Behavior

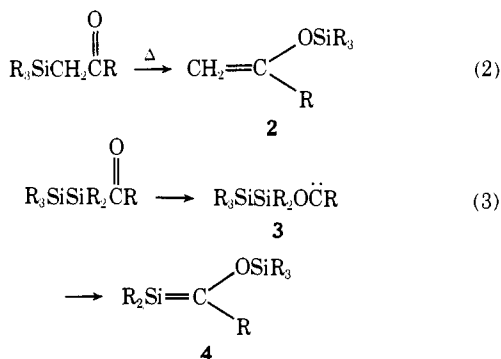
Sir:

The transient existence of reaction species which formally are written containing a silicon-carbon double bond is now well established.¹ Since the groups attached to the ends of the bond have generally been restricted to hydrogen, methyl, phenyl, and halogen, the range of compounds reported, and perhaps also their chemical behavior, has been limited. We wish to report a synthetic route to species containing a silicon-carbon double bond which have rather different substituents, and which display previously unreported behavior.

Based on the analogies of the thermal² and photochemical³ rearrangements of acylsilanes to siloxycarbenes,⁴ **1** (eq 1),



which insert into adjacent C-H bonds to give siloxyalkenes, and the thermal rearrangements of β -ketosilanes to siloxyalkenes⁵, **2** (eq 2), the thermolysis of acyldisilanes might be



expected to give rise to disilyloxycarbenes, **3**, or to species containing a silicon-carbon double bond, **4**, or both (eq 3). Despite the fact that β -ketosilanes do not normally undergo facile photochemical rearrangement,⁶ we found that the photolysis of several acyldi- or polysilanes proceeded cleanly to give products related to **4**.

Thus benzoyltris(trimethylsilyl)silane,⁷ **5**, λ_{max} (C_6H_{12}) 423 nm when photolyzed as a 0.035 M solution in dry methanol containing a trace of pyridine for about 30 min under N_2 at 10° using a 100-W Par 38 mercury spotlight, gave, by the expected addition of methanol across the Si-C double bond of **6**, the product **7** in 95% yield: (NMR (CCl_4) δ 7.01–7.25 (5 H, m, Ph), 4.85 (1 H, s, PhCH), 3.31 (3 H, s, OCH_3), 0.083 (9 H, s, OSiMe_3), 0.00 (18 H, s, SiMe_3); mass spectrum m/e 384 (M^+) absent, but m/e 365 ($\text{M} - \text{Me}$)⁺ observed⁷). No reaction occurred in the dark. Partial reduction of **7** with LiAlH_4 in ether at room temperature gave **8** (ir (CCl_4) 4.48 (SiH) μ ; NMR (CCl_4) δ 7.07–7.27 (5 H, m, Ph), 4.98 (1 H, d, $J = 3$ Hz, PhCH), 3.31 (1 H, d, $J = 3$ Hz; SiH), 0.10 (9 H, s, SiMe_3), 0.07 (9 H, s, SiMe_3), 0.00 (9 H, s, SiMe_3); m/e 354 (M^+)⁷).

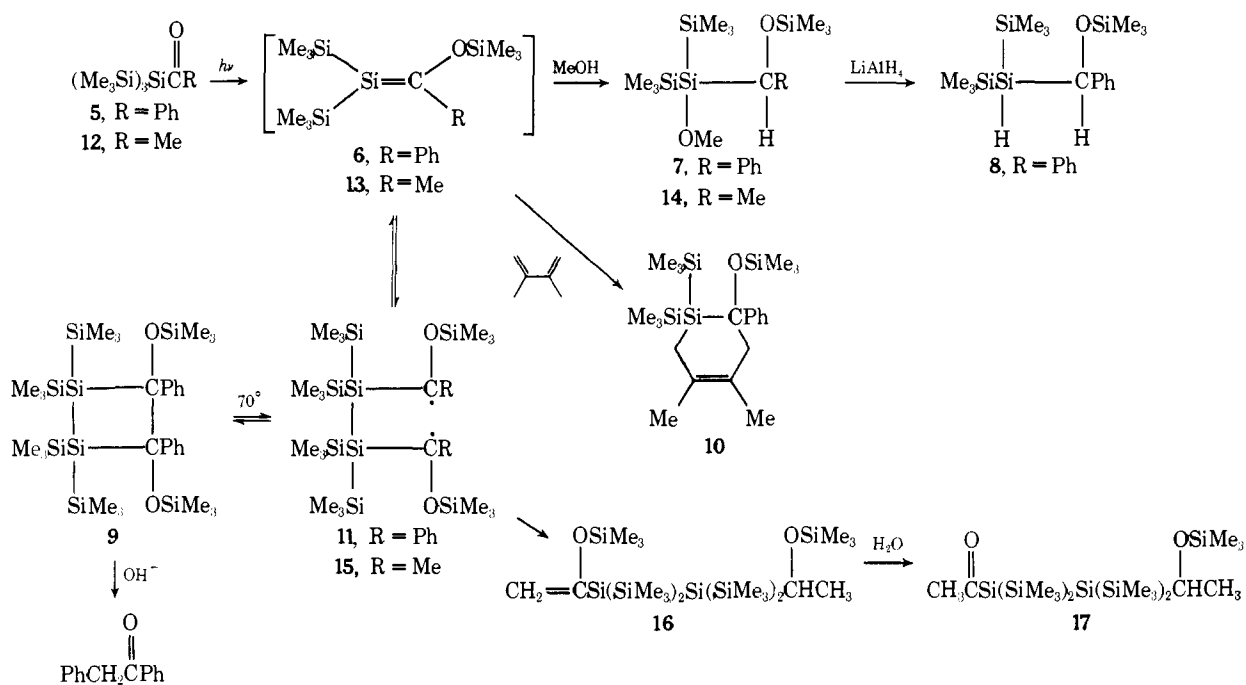
When photolyzed in ether, **5** gave rise in 70% yield to a dimeric species assigned the structure **9**, mp 149 – 150° (NMR (CCl_4) δ 7.13–7.73 (10 H, m, Ph), 0.40 (18 H, s, Me_3Si) 0.07 (18 H, s, Me_3Si), -0.27 (18 H, s, Me_3Si); mol wt, calcd 704, found 701 (osmometry); mass spectrum m/e 704 (M^+) absent, m/e 352 ($\text{M}^+/2$) (**6**), 337 (base peak) ($(\text{M}/2) - \text{Me}$)⁺).⁷ The assignment of the unusual head to head structure rests in part on the room temperature hydrolysis of **8** in 0.05 M NaOH in water, methanol, and ether to give siloxane material and benzyl phenyl ketone (90%), identified by spectra and mixture melting

point. While at least one rational pathway exists whereby **9** can yield benzyl phenyl ketone, no such pathway is obvious for the transformation of a head to tail dimer to this product.

Dimer **9** readily decomposes at 70° over 24 h in THF-methanol (3:1) giving **7** in at least 70% yield, but the dimer is not consumed in refluxing THF alone over the same time span, which strongly suggests that under these conditions a dimer-monomer ($\mathbf{9} \rightleftharpoons \mathbf{6}$) equilibrium exists. When refluxed in THF containing dimethylbutadiene, the silacyclohexene, **10**, expected from Diels-Alder trapping of **6**, was isolated in 71% yield: NMR (CCl_4) δ 7.00–7.35 (5 H, m, Ph), 2.70 (2 H, m, $\text{CH}_2\text{C}=\text{C}$), 1.73 (6 H, m, $\text{MeC}=\text{CMe}$), 1.40 (2 H, m, $\text{Si-CH}_2\text{C}=\text{C}$), 0.10 (9 H, s, Me_3Si), -0.03 (9 H, s, Me_3Si), -0.20 (9 H, s, Me_3Si); m/e 434 (M^+).⁷ The same adduct was formed when **5** was irradiated in ether for about 1 h in the presence of dimethylbutadiene, confirming the intermediacy of **6** in the photolysis.

The dissociation of **9** driven by relief of steric and ring strain, probably proceeds by homolytic fission of the carbon-carbon bond, to give the diradical **11** (dissociation of bisilylated tetraphenylpinacol to radicals at 80° in benzene is a pertinent analogy⁸). Evidence for the diradical **11** is found from the similar long-lived ESR spectra obtained at 0° , either when the acylsilane **5** is photolyzed in inert solvents in the ESR cavity or when a solution of **9** in a sealed tube and heated to 90° is transferred to the spectrometer. The spectra, primarily consisting of a quartet (J 4 G) of triplets (J 1.5 G) with a g value of 2.0077, is consistent with a disubstituted benzylic type radical.

Several acyldisilanes, when photolyzed in methanol-THF, gave similar behavior to that described above, suggesting the formation and trapping of silicon-carbon double bonded species. In addition, acetyltris(trimethylsilyl)silane,⁷ **12**, λ_{max} (C_6H_{12}) 368, gave the adduct **14** expected from trapping of compound **13** with methanol. Reduction of **14** gave the expected silane (analogous to **8**).⁷ When photolyzed in ether, **13** evidently dimerizes to the diradical **15**, which instead of ring-closing, undergoes disproportionation to give dimer **16** in 74% yield: NMR (C_6H_6) δ 4.82 (1 H, d, $J = 2$ Hz, $\text{HC}=\text{C}$), 4.62 (1 H, d, $J = 2$ Hz, $\text{HC}=\text{C}$), 4.42 (1 H, q, $J = 7$ Hz, MeCH), 1.57 (3 H, d, $J = 7$ Hz, MeCH), 0.40 (9 H, s, Me_3Si), 0.38 (27 H, s (2 overlapping signals), Me_3Si), 0.22 (9 H, s, Me_3Si), 0.15 (9 H, s, Me_3Si); mass spectrum m/e 580 (M^+)



absent, 565 (M - Me)⁺, 507 (M - Me₃Si)⁺.⁷ Hydrolysis in an acetone-methanol-pyridine-water solution of ammonium chloride gave the acyl disilane silyl ether **17** in 54% yield (ir (CS₂), 6.13 (C=O) μ ; NMR (C₆H₆) 4.37 (1 H, q, *J* = 7 Hz, MeCH), 2.27 (3 H, s, MeCO), 1.50 (3 H, d, *J* = 7 Hz, MeCH), 0.38 (9 H, s, SiMe₃), 0.37 (27 H, s, SiMe₃), 0.15 (9 H, s, SiMe₃); mass spectrum *m/e* 508 (M⁺) absent, 493 (M - Me)⁺, 435 (M - Me₃Si)⁺), confirming the head to head coupling of the silicon ends of the silicon-carbon double bond.

The findings demonstrate that silicon-carbon double bonds can be generated under relatively mild conditions (photochemically $\lambda > 360$ nm, thermally *T* \approx 70 °C), milder than hitherto reported, and, with the substituents here employed, that new and different chemical behavior results. We are continuing this research in directions we hope will further stabilize the transient intermediate.

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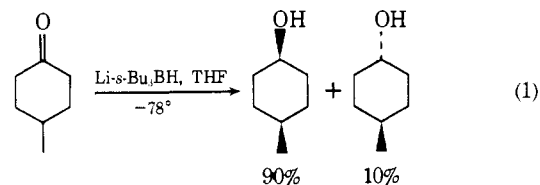
Lithium Trisiamylborohydride. A New Sterically Hindered Reagent for the Reduction of Cyclic Ketones with Exceptional Stereoselectivity

Sir:

Lithium trisiamylborohydride (LTSBH), a highly hindered trialkylborohydride, containing three β -methyl substituted

secondary alkyl groups,¹ the first reagent of its kind to be reported, reduces rapidly and quantitatively unhindered cyclic and bicyclic ketones with exceptional steric control. Thus, 3-methyl- and 4-*tert*-butylcyclohexanones are quantitatively converted to *trans*-3-methylcyclohexanol and *cis*-4-*tert*-butylcyclohexanol, respectively, in greater than 99.5% isomeric purity. The stereoselectivity achieved with this new reagent is far superior to any of the reducing systems currently available. Further, the reagent exhibits certain unique characteristics quite different from all of the previously examined trialkylborohydrides attributed to the exceptionally large steric requirements resulting from the presence of the three bulky alkyl substituents on boron.

In 1972 we reported that lithium tri-*sec*-butylborohydride (L-Selectride) reduces cyclic and bicyclic ketones with remarkable stereoselectivity.^{2,3} Since then numerous applications of this reagent in stereoselective organic synthesis (especially with prostaglandins) have appeared.⁴ However, there is one disadvantage to this reagent. Although 2-methylcyclohexanone is reduced to *cis*-2-methylcyclohexanol in 99.3% purity, the reduction of 3- and 4-alkyl-cyclohexanones proceeds with only 90-95% stereoselectivity (eq 1). It becomes a tedious task to remove the minor component at this level. It would be desirable to have a reagent that would improve the stereoselectivity of such transformation to 99% or better.



Recent developments in the hydroboration area have made available a number of hindered trialkylboranes.^{5,6} Now these can be readily and cleanly converted to the corresponding trialkylborohydrides. Accordingly, we examined a number of borohydride anions derived from such prospective derivatives (*B*-cyclopentyl-9-BBN, *B*-3-pinanyl-9-BBN, *B*-thexyl-9-BBN, tricyclohexylborane, hexyllimanylborane, etc.). Each of these derivatives was tested toward 2-methylcyclohexanone and 4-*tert*-butylcyclohexanone for their stereoselectivity. Of these, the selectivity exhibited by two reagents—lithium trisiamylborohydride and lithium tris(*trans*-2-methylcyclopentyl)borohydride (LTMBH)—were especially promising, far superior to any of the reagents currently available. Both of them have three bulky β -methyl substituted secondary alkyl groups on boron. A detailed comparative study of these two reagents revealed that LTSBH exhibits significant superiority over LTMBH (Table I).

Lithium trisiamylborohydride is conveniently prepared in

Table I. Reduction of Representative Cyclic and Bicyclic Ketones with Lithium Tris(*trans*-2-methylcyclopentyl)borohydride and Lithium Trisiamylborohydride in Tetrahydrofuran^a

Ketone	Temp, ^b °C	Less stable isomer	Isomer, %	
			Li-s-Bu ₃ BH	LiSi ₃ BH
2-Methylcyclopentanone	0	Cis	98.5	99.5
2-Methylcyclohexanone	0	Cis	99.3	>99.5
3-Methylcyclohexanone	-78	Trans	95.0	99.0
4-Methylcyclohexanone	-78	Cis	90.0	98.0
4-Ethylcyclohexanone	-78	Cis		99.0
4-Isopropylcyclohexanone	-78	Cis		99.0
4- <i>tert</i> -Butylcyclohexanone	-78	Cis	96.5	99.4
Norcamphor	0	Endo	99.6	99.7
Camphor	0	Exo	99.6	99.5 ^d
	25		99.0	99.3 ^f

^a Reactions were carried out essentially with stoichiometric quantity of reagents; total yield of the alcohols were $\geq 95\%$ determined by GLC using a suitable internal standard. ^b Reactions at 0° were run for 1 h and those at -78° for 2 h except otherwise stated. ^c *cis*-4-*tert*-Butylcyclohexanol was isolated in 98% yield. ^d 24 h at 0°. ^e Essentially inert at 0° in 2 h. ^f 80% conversion in 72 h at 25°.