Hamiltonian acting during t_1. This modulation is monitored by mixing the coherence back to observable magnetization with the propagator V and detecting during t_2. Fourier transformation of $S(t_1,t_2)$ gives the homogeneous spectrum along the ω_1 axis. No 2-D data manipulation is necessary, and in fact the spectrum of Figure 1b was taken with sampling at $t_2 = 0$ only. The multidimensional analogue of total spin coherence transfer echo spectroscopy would correspond to a projection[5] of cross peaks which correlate the total spin transition with other totally symmetric transitions. When $n \neq 1$ this would involve collecting data over two variable time dimensions in addition to t_2. The sequence presented here shows that this or any other projection is unnecessary.

The method is limited by the necessity of exciting the total spin coherence of the coupled system. To date, this has been achieved for more than a few spins only in oriented molecules.[7,10] In addition lines which belong to an uncoupled subsystem or to other than the totally symmetric irreducible representation do not appear. This can be both an advantage and disadvantage. Resolution is increased, but information is lost that would be available in a perfect magnet, e.g., the shift difference between different uncoupled subsystems.

The propagator U may be as simple as the sequence $(\pi/2)$-$(\tau/2)$-π-$(\tau/2)$-$(\pi/2)$ or may be a selective excitation sequence.[10] The other propagators may be single pulses or more elaborate and selective pulse sequences. For the single quantum case ($n = 1$), no mixing is necessary between t_1 and t_2 and Figure 1b was obtained with $V = 1$. When $n \neq 1$ an advantage of more elaborate mixing propagators is that *properly phased lines* of known relative amplitude and homogeneous width may be obtained for multiple quantum transitions. Modulation of the relative rf phases of the propagators allows complete separation of the desired transitions of different orders and eliminates artifacts arising from nonidealities of the pulse sequence.[8] Quantitative aspects of line intensities, phases, widths, separation techniques, and the role of diffusion will be presented in a full paper.

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6-Silafulvene via Silylcarbene Rearrangement from Diazo-2-silacyclohexa-3,5-diene

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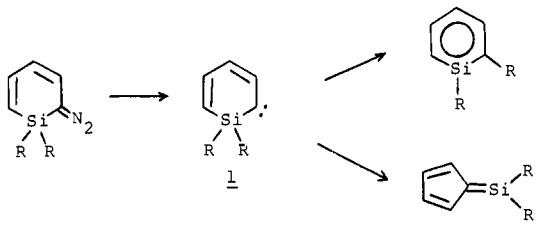
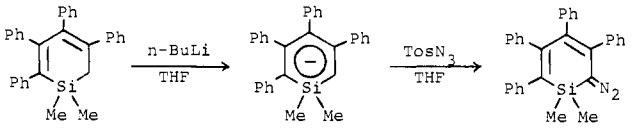
Both silabenzene and silafulvene are attractive molecules in silicon chemistry. The thermally induced retroene route to silabenzene has recently employed by the Barton group,[1] and the existence was confirmed by matrix method at low temperature.[2] More recently, evidence for the intermediacy of 6-silafulvene by retroene reaction was also presented independently by the groups of Barton and Sakurai.[3]

We have reported that α-silylcarbenes undergo 1,2 migration of the substituent from silicon to a carbene center to give reactive silicon–carbon double-bonded intermediates.[4] A failed attempt to obtain silabenzene by 1,4-methyl migration of 4,4-dimethyl-4-silacyclohexadienylidene was reported.[5] One might expect that 2,2-dimethyl-2-silacyclohexadienylidene (**1**) would give silabenzene or/and 6-silafulvene by 1,2 migration of the substituent. We



present here strong evidence for the generation of 6-silafulvene from the reaction of diazo-2,2-dimethyl-3,4,5,6-tetraphenyl-2-silacyclohexa-3,5-diene (**2**).

Synthesis of **2** was by a modification of the original method of Doering and Depuy.[6] Treatment of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclohexa-2,4-diene (7.0 g, 16.4 mmol) with equimolar *n*-butyllithium in THF at 0 °C formed the red silacyclohexadienyl anion immediately.[7] Addition of the anion to a solution of *p*-toluenesulfonyl azide (3.9 g, 19.8 mmol) in THF at −77 °C produced, upon workup, **2** in 36% yield. The yellow



crystalline diazo compound **2** was stable enough to be recrystallized, mp 134.5–135.5 °C dec; NMR (CCl_4, δ) 0.43 (s, 6 H, $SiMe_2$) and 6.37–7.33 (m, 20 H, ArH); IR (KBr) 2030 (N_2) and 1260 cm^{-1} (SiMe); mass spectrum, *m/e* 426 ($M^+ - 28$).

When a benzene solution of **2** (252 mg, 0.556 mmol) containing excess *tert*-butyl alcohol was refluxed in a sealed Pyrex tube at ca. 100 °C in the presence of catalytic amount of anhydrous cupric sulfate (57 mg), vigorous reaction occurred and ceased in a few minutes. Separation of the reaction mixture by silica gel chromatography gave cyclopentadienyl-*tert*-butoxysilane **4** in 96% yield as white crystals, mp 147–148 °C; NMR (CCl_4, δ) −0.23 (s, 6 H, $SiMe_2$), 0.80 (s, 9 H, *t*-Bu), 4.63 (s, 1 H, SiCH), and 6.83–7.40 (m, 20 H, ArH); IR (KBr) 1240 (SiMe) and 1050 cm^{-1} (SiOC); mass spectrum, *m/e* 500 (M^+). The upfield shift of the silyl methyl groups was observed by the shielding effects of the two phenyl rings at the 1 and 4 positions.

The formation of **4** provides strong evidence for 1,2,3,4-tetraphenyl-6,6-dimethyl-6-silafulvene (**3**) by the migration of the dienyl group to the carbene center. It seems reasonable that the dipolar form of the silafulvene would have enhanced importance because of the stability of the cyclopentadienyl anion. No product from 1,2-dimethyl-3,4,5,6-tetraphenyl-1-silabenzene by the methyl migration was found.

The evidence for the silafulvene **3** was further substantiated by similar reactions with methanol and methanol-*d*. The reaction of **2** with methanol gave 1,2,3,4-tetraphenyl-1,3-cyclopentadiene (**6**)[8] in 91% yield, mp 177–178 °C, probably formed by metha-

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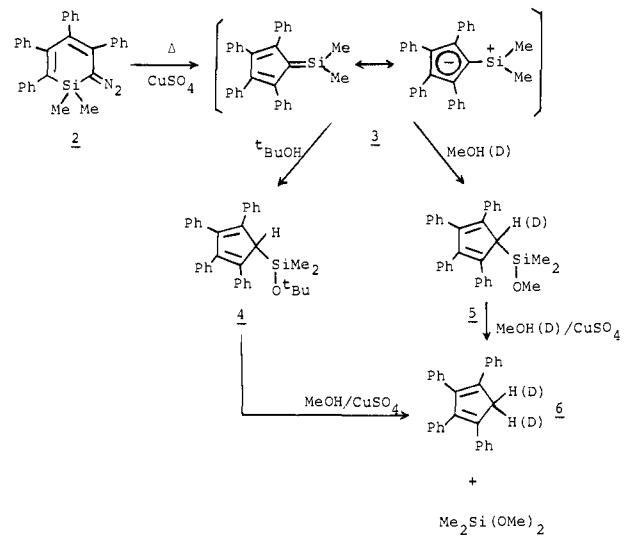
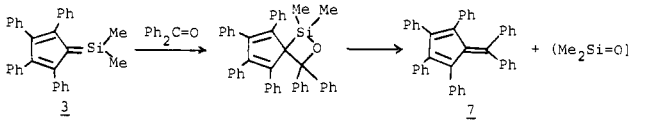


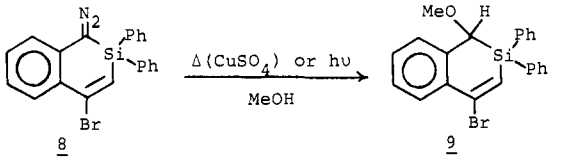
nolysis of the cyclopentadienylmethoxysilane **5**. The cyclopentadienyl-*tert*-butoxysilane **4** was found to give the desilylated cyclopentadiene **6** in 96% yield under the reaction conditions. The reaction of **2** with methanol-*d* led to the formation of 1,2,3,4-tetraphenyl-5,5-dideuterio-1,3-cyclopentadiene in 95% yield, mp 177–178 °C; mass spectrum, *m/e* 372 (M^+); and in its NMR spectrum the peak at δ 3.97, attributed to the methylene protons of the cyclopentadiene, was completely absent.

A benzene solution of **2** containing excess benzophenone was subjected to thermolysis at ca. 100 °C in the presence of anhydrous cupric sulfate to afford 1,2,3,4,6,6-hexaphenylfulvene **7**[9] in 66% yield as almost black crystals.[10] The formation of the fulvene



7 indicates 6-silafulvene **3** as an intermediate in the reaction of **2**. It is well documented that silicon–carbon double-bonded intermediates react with carbonyl compounds to give silaoxetanes which decompose to olefins and silanones.[11] Similar reaction of **2** with benzaldehyde produced 1,2,3,4,6-pentaphenylfulvene as rust-red crystals.[9] These results demonstrate that the reaction of **2** occurred only in the direction that forms the silafulvene **3** which was successfully trapped by alcohols and carbonyl compounds.

However, the reaction of silyl diazo compound **8**[12] was quite different from that of **2**. A simple OH insertion product **9**[13] was



obtained in 96% yield when benzene–methanol solution of **8** was refluxed at ca. 100 °C for 5 min in the presence of anhydrous cupric sulfate. The photochemical decomposition of **8** in methanol–benzene also produced the product **9**. Further investigation of the silafulvene as well as the chemistry of silabenzene is now in progress.

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Bifunctional Chiral Synthons via Microbiological Methods. 1. Optically Active 2,4-Dimethylglutaric Acid Monomethyl Esters

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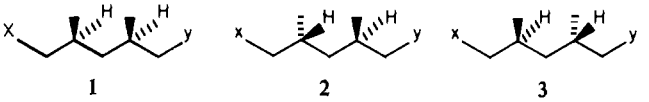
In recent years, the "polyoxo" macrolide aglycons[1,2] and other multifunctional macrocyclic compounds such as the maytansines,[3,4] ansa antibiotics,[5,6] and ionophores[7-9] have attracted the attention of many synthetic chemists. Most of the approaches used in the construction of acyclic chains with multiple chiral centers entailed the successive assembly of a series of prefabricated optically active building blocks containing the desired stereochemical functional features of the intended synthetic targets. For example, (*S*)-β-hydroxyisobutyric acid[10] has been used extensively as a starter chiral unit, which has greatly facilitated the design and execution of several total syntheses.[6-8,11] Herein, we report the preparation of three bifunctional chiral synthons, **1-3** representing partial



1 2 3

X = CO_2CH_3; Y = CO_2H

structural units, commonly encountered in macrolide[1,2] and polyether[7-9] antibiotics.

We had previously demonstrated the enantiotopic specificity of pig liver esterase[12] (PLE), which catalyzed the stereospecific hydrolysis of the pro-*R* ester grouping in dimethyl β-hydroxy-β-methylglutarate. Chemoselective reduction of either the acid or ester functionality in the resulting product afforded (*R*)- and (*S*)-mevalonic acids, respectively. Because PLE has a relatively

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(12) Silyl diazo compound **8** was prepared by the oxidation of the hydrazone from the corresponding silyl ketone with mercuric oxide, orange-yellow crystals, mp 129–130 °C; NMR (CCl_4, δ) 6.70–8.17 (m, ArH and BrC=CHSi); IR (KBr) 2030 cm^{-1} (N_2). Anal. Calcd for $C_{21}H_{15}N_2SiBr$: C, 62.53; H, 3.74; N, 6.94; Br, 19.81. Found: C, 62.47; H, 3.69; N, 7.05; Br, 20.10.
(13) NMR (CCl_4, δ) 3.27 (s, 3 H, OMe), 4.63 (s, 1 H, SiCHO), and 6.87–7.90 (m, 15 H, ArH and BrC=CHSi); mass spectrum, *m/e* 406 (M^+, ^{79}Br) and 408 (M^+, ^{81}Br).

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