$Fe_3(CO)_{12}$ also shows high initial activity which diminishes during the sonication. In this case, however, no iron species other than $Fe_3(CO)_{12}$ are detected even after prolonged sonication. As shown in Table II, the rate of 1-pentene isomerization can be enhanced by $>10^5$ by sonolysis of the iron carbonyls.

In the photocatalyzed isomerization of 1-pentene by $Fe(CO)_5$, the catalytically active species is proposed[15,16] to be $Fe(CO)_3$(pentene) which is obtained by sequential photodissociation of CO in the presence of pentene. Isomerization would then occur via β-hydrogen abstraction, forming $Fe(CO)_3(H)$(1-ethyl-π-allyl) which produces the 2-pentenes. A similar mechanism has been demonstrated[17] for the thermal catalysis of olefin isomerization by $Fe_3(CO)_{12}$. In the photocatalysis by both $Fe(CO)_5$ and $Fe_3(CO)_{12}$ the trans/cis ratio of the 2-pentene produced is always ~ 3, which is consistent with a common, mononuclear catalytic species.[18] The sonocatalysis produces the same trans/cis ratio, which does not change during sonication, as expected if the same catalysis species is produced.

Ultrasonic cavitation creates extremely intense thermal heating but for only very brief (submicrosecond) duration. This can produce unusual chemistry, distinct from both photochemical and thermal processes. The use of high-intensity ultrasound to initiate ligand dissociation is a novel method of catalyst activation with unique potential. The potential ability to induce ligand dissociation from complexes inert to photochemical or low-energy (<200 °C) thermal processes suggests that sonocatalysis may be produced by intermediates not normally accessible. Further work is in progress to explore this hypothesis.

Acknowledgment. This work was supported by a Cottrell grant from the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE-8020006).

Registry No. $Fe(CO)_5$, 13463-40-6; $Fe_2(CO)_9$, 15321-51-4; $Fe_3(CO)_{12}$, 17685-52-8; 1-pentene, 109-67-1; *cis*-2-pentene, 627-20-3; *trans*-2-pentene, 646-04-8.

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1-Silacyclopent-3-en-1-ylidene, a Cyclic Silylene from the Reactions of Silicon Atoms, and a Silicon Atom Synthon[†,‡]

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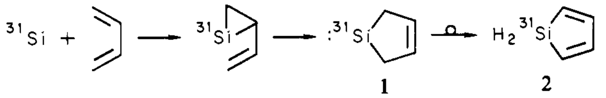
The suggestion that 1-silacyclopent-3-en-1-ylidene (**1**) is produced as a reactive intermediate from recoiling silicon atoms and 1,3-butadiene has been made to explain the formation of 1-silacyclopenta-2,4-diene (**2**).[1-3]

$$PX_3 + n \longrightarrow {}^{31}Si + p + 3X \qquad (X = H, F)$$



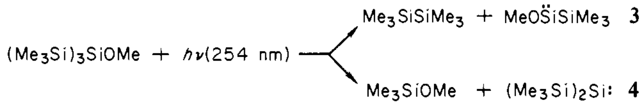
1 **2**

Since unsubstituted silole **2** has *not* been prepared by other means,[4-6] its identification as a product in hot-atom experiments remains, in our view, controversial.[2,5]

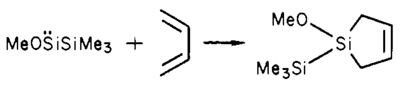
It has now been possible, however, to generate silylene **1** directly, and it reacts with butadiene to form in high yield a product which we have also found from recoiling silicon atoms and from the cocondensation of silicon vapor with the same substrate. We are thus reporting new evidence for the intermediacy of 1-silacyclopent-3-en-1-ylidene (**1**) in the reactions of silicon atoms, the first fruitful reaction of thermally evaporated silicon with a hydrocarbon, and a silicon atom synthon.

1-Silacyclopent-3-en-1-ylidene (**1**) was produced by pyrolysis of 1-methoxy-1-(trimethylsilyl)-1-silacyclopent-3-ene (**5**). This silylene precursor was itself the product of a silylene reaction in the photolysis of methoxytris(trimethylsilyl)silane in butadiene solution.

While the photochemistry of alkyl- and mixed alkylarylpolysilanes has received considerable attention,[7,8] this seems to be the first report of the photolysis of an alkoxypolysilane. In this case, photoinduced α elimination is nonspecific, forming both methoxy(trimethylsilyl)silylene (**3**) and bis(trimethylsilyl)silylene (**4**) in ca. 2:1 ratio.[9] The trapping of silylenes by 1,3-dienes to give 1-silacyclopent-3-enes is well established.[7,10,11]



$$(Me_3Si)_3SiOMe + h\nu(254\text{ nm}) \longrightarrow \begin{cases} Me_3SiSiMe_3 + Me\ddot{O}SiSiMe_3 & \mathbf{3} \\ Me_3SiOMe + (Me_3Si)_2Si\colon & \mathbf{4} \end{cases}$$



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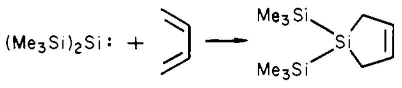

6

In a typical experiment 49% of **5** and 23% of the bis(trimethylsilyl)silacyclopentene (**6**) were obtained, together with 17% recovered methoxytris(trimethylsilyl)silane.

When such a reaction mixture, containing excess butadiene, was heated at 310 °C for 2.5 h following 6 h of irradiation, **5** underwent thermally induced α elimination which was, as expected, specific to the removal of methoxytrimethylsilane. Reaction of the resulting cyclic silylene **1** with butadiene gave the spiro adduct 5-silaspiro[4.4]nona-2,7-diene (**7**), a known compound,[12] in 32% overall yield.[13]

The spiro compound **7** is also formed in low (ca. 0.5%) yield in the gas phase from reactions of recoiling ^{31}Si atoms in mixtures of phosphine and butadiene. It had previously eluded detection recoil experiments[2] but has now been identified by comparison

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[†] We dedicate this communication to George Hammond with gratitude for the inspiration, both human and scientific, that he has always provided.

[‡] This research has been made possible by financial support from the United States Department of Energy. This is technical report COO-1713-98.

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[13] The bis(trimethylsilyl)silacyclopentene (**6**) also present was stable under the reaction conditions. Its yield actually increased slightly due to pyrolysis of the small amount of remaining methoxytris(trimethylsilyl)silane exclusively to **4** that underwent addition to butadiene.

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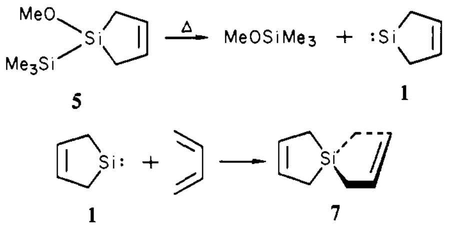


5 1

1 7

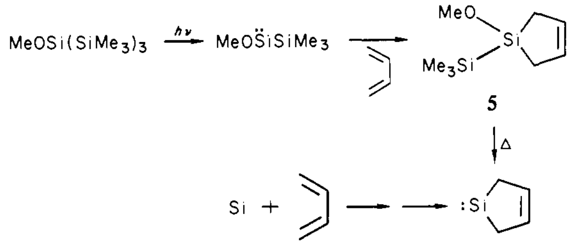
of its vapor chromatographic retention times with those of an authentic sample[12] on three columns of widely varying retention characteristics.[14]

The spirosilanonadiene **7** has also been found as the only volatile product detected from the cocondensation of silicon vapor with butadiene in a Timms "freeze-fry" metal evaporation apparatus[15] modified to reach the ca. 1600 °C required for vaporization of silicon.[16] While the yield was again low (ca. 1%), this is the first stable product obtained from cocondensation of silicon vapor with a hydrocarbon.

Although its yield from the hot atom experiments is small, the detection of **7**, an unambigously identified product that is formed in >50% yield (based on the immediate silylene precursor) from 1-silacyclopent-3-en-1-ylidene (**1**) and butadiene supports the view that this cyclic silylene is an intermediate in the recoil reactions. We have also found two other as yet unidentified products in higher yield (ca. 5%) whose chromatographic behavior suggests that they are $^{31}SiC_8$ compounds. While these may turn out to be rearrangement products of the spiro silanonadiene **7**, there is the more interesting possibility that they are cycloadducts of rearrangement products of the cyclic silylene **1**. The gas-phase rearrangements of **1** are presently under investigation.

The formation of spirosilanonadiene **7** from cocondensation of silicon vapor and butadiene also implies the intermediacy of silacyclopentenylidene (**1**), since silicon vapor is known to be principally monatomic.[16] Even the low product yield obtained raises the question whether "direct synthesis"[17] of organosilanes is possible via monoolefins.

Finally it is worth noting that, in a two-step process, all the



5

1

appendages to the central silicon atom of methoxytris(trimethylsilyl)silane have been removed, and the same end product obtained as arose in much lower yields from recoiling silicon atoms and silicon vapor. Thus both the methoxytris(trimethylsilyl)silane and the methoxy(trimethylsilyl)silylene may be viewed as synthetic equivalents of a silicon atom.

Acknowledgment. We are grateful to the United States Department of Energy for support of this research. This is technical report C00-1713-98. We thank John Hood and the Washington University Cyclotron for fast neutron irradiations and the Washington University Cyclotron Machine Shop for fabrication of the metal evaporation apparatus.

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(14) Retention times at 80 mL/min of He flow, $^1/_4$-in. columns, 10% W/W stationary phase on 40–50 mesh Anakrom ABS: 35 min on 20-ft SF96 silicone oil, 125 °C; 14.5 min on 20-ft carbowax 20M, 130 °C; 19 min on 15-ft tricresyl phosphate, 110 °C.

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(16) Ca. 150 mg of silicon was evaporated within a period of 15 min from a beryllia crucible supported within a tungsten spiral through which a current of 76 A at 9.5 V was passed. Silicon vapor at 1660 K is reported to consist of 94% Si_1, 3% Si_2, 1.5% Si_3, 1% Si_4, and $^1/_2$% $Si_{>4}$. R. E. Honig, *J. Chem Phys.*, **22**, 1610 (1954).

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Lewis Acid Enhancement of Photochemical Trans → Cis Isomerization of α,β-Unsaturated Esters[1]

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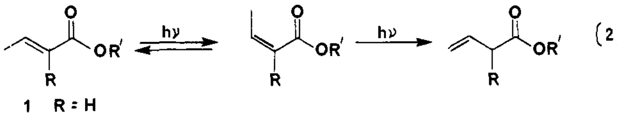
The photochemical cis–trans isomerization of alkenes has played a central role in the development of theoretical and mechanistic photochemistry.[2,3] Synthetic applications of this reaction[4] have been limited by its reversible nature, which, in the absence of other reactions, leads to a photostationary state mixture of isomers (eq 1). Photostationary states enriched in the thermodynamically

$$\frac{[\text{cis}]}{[\text{trans}]} = \frac{(\Phi_{t\to c})(\epsilon_t)}{(\Phi_{c\to t})(\epsilon_c)} \qquad (1)$$

less stable cis isomer can be obtained via direct irradiation if the trans isomer is more strongly absorbing than the cis isomer ($\epsilon_t > \epsilon_c$), as is the case for the stilbenes,[3] or via triplet sensitization if the triplet energy of the trans isomer is lower than that of the cis isomer, as is the case for β-ionol.[5] Unfortunately, neither direct nor triplet-sensitized irradiation provides a general method for the efficient conversion of trans to cis isomers. The use of various additives (protic acids,[6] copper salts,[7] metal carbonyls,[8] π acceptors,[9a] free radical precursors[9b]) and restricted environments[10] have also failed to yield cis-rich isomer mixtures. Cis–trans photoisomerization may be further complicated by competing reactions, such as the deconjugation of *cis*-crotonate (**1**) and angelate (**2**) esters (eq 2).[11] We wish to report that the irradiation



(2)

1 R = H
2 R = CH_3

of several α,β-unsaturated esters in the presence of Lewis acids leads to photostationary states enriched in the cis isomer, without substantial deconjugation in the case of esters **1** and **2**. The mechanistic basis for this novel and preparatively useful application of Lewis acids to organic photochemistry is an increase in both ϵ_t/ϵ_c and $\Phi_{t\to c}/\Phi_{c\to t}$ upon Lewis acid complexation of the α,β-unsaturated esters.

Irradiation of the trans α,β-unsaturated esters **1–7** in the absence of Lewis acids results in 5–49% optimum conversion to the cis isomers (conditions specified in Table I). A true photostationary state is obtained for esters **3–7** but not for esters **1** and **2** due to photochemical deconjugation as shown for ester **2** in Figure 1a. Irradiation of these esters in the presence of selected Lewis acids results in a substantial increase in the optimum conversion to the cis isomers and suppression of deconjugation,

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