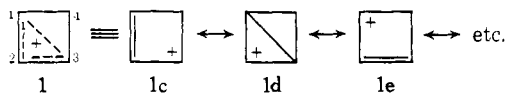


17 ppm) than C_1 and C_3 , although the magnitude of the shift difference is substantially reduced as the result of imposed geometric constraints making 1,3-orbital-interaction more favorable. The reversal of shifts again indicates that a considerable amount of positive charge has been delocalized onto C_2 in the cyclobutenyl cations **1** and **2**, *via* a strong 1,3-interaction. In addition, the one-bond $^{13}\text{C-H}$ coupling constants observed in the allylic fragment of these ions are unusually large (on the order of 230 Hz).¹¹ For example, the $J_{^{13}\text{C-H}}$'s for C_1 and C_3 (211.2 and 224.3 Hz for **1** and **2**, respectively) are larger than those of bridgehead positions in bicyclo[1.1.0]butane (205 Hz)¹² and the $J_{^{13}\text{C-H}}$'s for C_2 (236.3 and 230.6 Hz, respectively) are found to approach those of the recently reported cyclopropenium ion.¹³ The $J_{^{13}\text{C}_1-\text{H}}$ of **1** is found to be substantially smaller than that of **2** and is not unexpected as increasing geminal substituent electronegativity has been demonstrated to result in increased $J_{^{13}\text{C-H}}$'s.¹²

Although the unusual deshielding at C_2 and shielding at C_1 , C_3 alone would indicate that structure **1d** is a significant contributor to **1**, the unusually large $J_{^{13}\text{C-H}}$'s and temperature-dependent pmr spectra observed for **1** indicate that the cyclobutenyl cation (*planar*) approaches the truly homocyclopropenyl-type geometry (*nonplanar*) **1a** (or **1b**) with the $C_1-C_2-C_3$ angle intermediate between 60 and 90°. Vicinal, *cis* vinylic

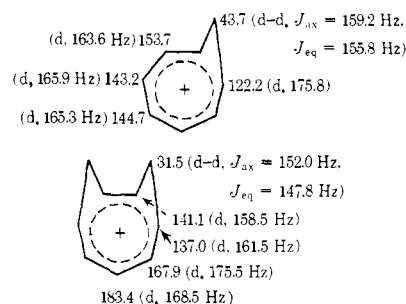


proton coupling constants have been shown to depend on ring size, the magnitude decreasing monotonically with reduction of ring size.^{12d} In the pmr spectra of **1** and **2**, $J_{1,2}$ (1.60 Hz) is much smaller than that observed in cyclobutene systems ($J_{1,2} = 2.5\text{--}3.7$ Hz) and approaches that of a cyclopropenyl system ($J_{1,2} = 0.5\text{--}1.5$ Hz). In addition, the $J_{^{13}\text{C-H}}$'s observed for C_1 , C_2 , and C_3 in **1** and **2** bear a good resemblance to that observed in the cyclopropenyl cation.¹³ Increasing $J_{^{13}\text{C-H}}$ values for small-ring compounds have been shown to correlate at least qualitatively with increased ring strain¹² (according to decreasing ring size). For example, the $J_{^{13}\text{C-H}}$'s for the vinylic carbons in cyclopropene and cyclobutene are 220 and 170 Hz, respectively.¹² Moreover, the pentamethyl- and 1,2,3,4-tetramethylcyclobutenyl cations reported by Katz^{2a,b} have been shown to be allylic ions with an unusually significant 1,3-orbital interaction, which, because of the geometric constraints of the four-membered ring, render the 1,3-distance unusually small. In the unsubstituted, parent cyclobutenyl cation **1**, and the 4-

chloro-substituted analog **2**, the much stronger 1,3-interaction should make the 1,3-distances even shorter and consequently result in the bending of the molecule necessitated to relieve ring strain. A related, well-known example is that of the homotropylium cation in which strong 1,7-orbital overlap (intermediate between σ and π) renders the ion *nonplanar*.¹⁵ The magnetic nonequivalence of the methylene protons in the homotropylium cation allows measurement of the rate of the ring-inversion process. The strong 1,3-orbital interaction in the cyclobutenyl cations **1** and **2** should also involve overlap intermediate between σ - and π -bonding nature, resulting in the nonplanarity of these ions.¹⁸ We, therefore, conclude that the presently studied cyclobutenyl cations **1** and **2** should indeed be considered as monohomocyclopropenyl cations with ring deformation. The homoaromaticity predicted for the homocyclopropenyl cation is thus explicitly established. Ion **1** is the homoaromatic analog of Breslow's cyclopropenyl cation,¹³ and thus the simplest possible homoaromatic system.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

(15) We have previously reported the carbon shifts for both the mono- and bishomotropylium ions.¹⁶ We have now also obtained the carbon-hydrogen coupling constants for these ions from the proton



coupled CFT spectra. Although a recently published explanation for homoaromatic stability proposes that homotropylium ions might be stabilized through a Möbius structural arrangement (eight electrons) rather than a Hückeloid type (six electrons),¹⁷ the observed coupling constants indicate no appreciable cyclopropane ring formation.

(16) G. A. Olah, G. Liang, L. A. Paquette, M. J. Broadhurst, and P. Warner, *J. Amer. Chem. Soc.*, **95**, 3386 (1973).

(17) W. J. Hehre, *J. Amer. Chem. Soc.*, **95**, 5807 (1973).

(18) Recently Lodder and Buck, *et al.*, reported a series of aryl substituted cyclobutenyl cations and they also have found, in one case, that 1,3-interaction, induced by unfavorable steric crowding, became important in 1,3-diphenyl-2-*tert*-butylcyclobutenyl cation, which showed a deshielded C_2 shift. See A. E. Lodder, J. W. Haan, L. J. M. Ven, and H. M. Buck, *Rec. Trav. Chim. Pays-Bas*, **92**, 1040 (1973).

George A. Olah,* John S. Staral, Gao Liang

Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106

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Chromium Carbonyl Photocatalyzed 1,4-Hydrosilation of 1,3-Dienes. A Synthesis of Allylsilanes

Sir:

We recently communicated¹ some characteristics of the $\text{Cr}(\text{CO})_6$ photocatalyzed hydrogenation of 1,3-dienes which may have synthetic utility. The reports²⁻⁴ that

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(11) Long range carbon-hydrogen coupling constants in **2** are $J_{C_1H_4} = J_{C_3H_4} = 6.5$ Hz, $J_{C_1H_2} = J_{C_3H_2} = 6.5$ Hz, $J_{C_2H_1} = J_{C_2H_3} = 7.2$ Hz, and $J_{C_4H_1} = J_{C_4H_3} = 6.5$ Hz.

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(13) R. Breslow, J. T. Groves, and G. Ryan, *J. Amer. Chem. Soc.*, **89**, 5048 (1967).

(14) Recent MINDO/2 and *ab initio* (4-31G) calculations have predicted the homocyclopropenyl cation to be nonplanar. (a) W. W. Schoeller and G. E. Schenck, *Tetrahedron*, **29**, 425 (1973); (b) A. J. P. Devaquet and W. J. Hehre, *J. Amer. Chem. Soc.*, **96**, 3644 (1974).

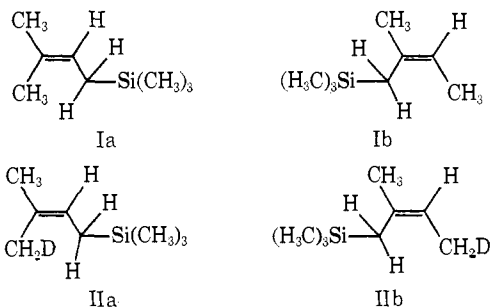
Table I. Allylsilanes Synthesized by $\text{Cr}(\text{CO})_6$ Photocatalyzed 1,4-Hydrosilation of 1,3-Dienes^a

Starting diene	Starting silane	Product(s)
	HSiMe_3	
	H_2SiPh_2	
	$\text{HSi}(\text{OEt})_3$	
	H_2SiMe_2	
	HSiMe_3	
	DSiMe_3	
	HSiMe_3	
	HSiMe_3	

^a These reactions are carried out on the neat substrates in approximately 1:1 mole ratios on an approximately 0.05 mol scale. The deoxygenated solutions are saturated in $\text{Cr}(\text{CO})_6$ and exposed for several days to the output of a black light equipped with two 15-W GE black light bulbs. The reaction temperature is approximately 30°. The products were generally identified by gc ($\beta\beta'$ -ODPN or OV-101 column), nmr, and ir spectra after distillation to remove catalyst and residual starting materials.

silanes containing an Si-H bond oxidatively add to photogenerated coordinatively unsaturated metal carbonyls has prompted us to explore the possibility of achieving 1,4-hydrosilation of 1,3-dienes using $\text{Cr}(\text{CO})_6$ as the photocatalyst. This communication describes the first synthetic application of transition metal photocatalysis: the conversion of 1,3-dienes to allylsilanes.

Near-uv photolysis (300–380 nm) at 25° of $\text{Cr}(\text{CO})_6$ in catalytic amounts in neat degassed solutions of a 1,3-diene and a silane having an Si-H bond (~1:1 mole ratio) gives 1,4-hydrosilation of the diene. The allylsilanes are obtained on a synthetic scale, and in many cases almost quantitative isolated chemical yields are obtained. Some representative starting materials and their products are given in Table I. Most of the products, especially those derived from HSiMe_3 , are identified unambiguously by their nmr spectra. For example, consider the allylsilanes Ia and Ib and IIa and IIb obtained from the reaction of 2-



methyl-1,3-butadiene and HSiMe_3 and DSiMe_3 , respectively. Along with the other nmr resonances in proper intensities, each of these products exhibits an absorption near τ 4.8 which integrates as one proton and is thus assigned as the vinyl proton: Ia, τ 4.81 (triplet); Ib, τ 4.80 (quartet); IIa, τ 4.84 (triplet); IIb, τ 4.85 (triplet). Thus, integration, position, and splitting are wholly consistent with the products as

shown. However, Ib, IIa, and IIb exist as cis-trans isomers. Evidence for the isomers shown comes from ir and gc data for reaction products of 1,3-butadiene (only one 1,4-hydrosilation product) and *trans*-1,3-pentadiene. Data for the ir spectra are available⁵ for both cis and trans isomers of the reaction product of HSiMe_3 and 1,3-butadiene and our values are in excellent agreement for the cis product. Additionally, the cis product is >99% isomerically pure as determined by gc under conditions where both cis and trans are well separated. There is no evidence for Si-containing products other than those indicated in Table I, and little or no detectable simple alkene (net hydrogenation) products are observed. We have been unable to detect reaction of HSiEt_3 with either *trans,trans*-2,4-hexadiene or *cis*-1,3-pentadiene. Selective (and complete) 1,4-hydrosilation of *trans*-1,3-pentadiene in the presence of an initially equivalent amount of either *cis*-1,3-pentadiene or *trans,trans*-2,4-hexadiene ensures that these two dienes are not inhibitors but are simply inert under the reaction conditions. Finally, in a practical sense, reaction times for good synthetic conversion vary considerably depending on light intensity, temperature, number of moles to be converted, etc. Some information along these lines is outlined below. The complexes $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ also function as photocatalysts for the hydrosilation reaction, but their known⁶ ability to also serve as olefin isomerization photocatalysts makes the $\text{Cr}(\text{CO})_6$ the photocatalyst of choice.

Photolysis of the $\text{Cr}(\text{CO})_6$ -1,3-diene-silane mixture is required to initiate the hydrosilation but continued photolysis is not required to sustain product formation as shown by data in Table II. Such data provide

Table II. $\text{Cr}(\text{CO})_6$ Photocatalyzed Reaction of $\text{HSi}(n\text{-Pr})_3$ and 2,3-Dimethyl-1,3-butadiene at Various Conditions

Time $h\nu$, hr (T , °C)	Time Δ , hr (T , °C)	% conversion to product
4 (10) ^a	0 (—)	0.45
4 (25) ^a	0 (—)	0.58
4 (60) ^a	0 (—)	1.32
7 (25) ^b	0 (—)	0.16
0 (—) ^c	200 (45)	0.00
7 (25) ^b	12 (45)	0.36
7 (25) ^b	36 (25)	0.38

^a Degassed, hermetically sealed, 3.0 ml of benzene solution, 0.5 M in diene, 0.5 M in silane, and 5.6×10^{-3} M in $\text{Cr}(\text{CO})_6$ exposed to black light (3.5×10^{-7} einstein/min incident on sample) under identical conditions except for temperature. ^b Same samples as in footnote a except diene and silane are each 1.0 M. Each sample here was irradiated simultaneously in a merry-go-round at 25° for 7 hr and then treated thermally as indicated. ^c Same sample as in footnote b.

compelling evidence to conclude that the reaction can be catalytic with respect to photons. The temperature dependence of the initial hydrosilation rate under continuous photolysis (Table II) is also consistent with a truly photocatalytic reaction; a situation where the role of the light is to generate a thermally active catalyst. However, in principle, photochemical acceleration may obtain for the general catalytic steps of metal-

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substrate complex formation, substrate reaction, and decomplexation of the transformed substrate. Thus, a rationale is provided for the observation that continuous illumination of the reaction mixture accelerates conversion to allylsilanes.

The catalytic reaction of the silanes and the dienes can also be achieved only thermally using (benzene)Cr(CO)₃ at temperatures utilized for 1,4-hydrogenation of 1,3-dienes by this catalyst.⁷ We find that both 2-methyl-1,3-butadiene and *trans*-1,3-pentadiene react with HSiEt₃ using (C₆H₆)Cr(CO)₃ at 175°. However, though the allylsilanes obtained are common to the Cr(CO)₆ photochemical procedure, we find that the products occur in different ratios and more importantly substantial yields of diene dimers are formed.

The similarity of the reactivity of H₂ or D₂^{1,8} and the Si-H in the Cr(CO)₆-1,3-diene system is remarkable; only 1,4-addition products obtain which are inert to further reaction; similar reaction is catalyzed thermally by (C₆H₆)Cr(CO)₃; *cis* double bonds are generated in the product; and apparently the *s-cis* conformation of the diene must be accessible (*e.g.*, selective reaction of *trans*-1,3-pentadiene in the presence of an equal amount of *cis*-1,3-pentadiene). One major difference, however, is the fact that hydrosilation does not readily proceed when a methyl substituent is in the 1 or 4 position of the 1,3-diene. Hydrogenation of *trans,trans*-2,4-hexadiene proceeds readily¹ but no reaction could be detected with HSiEt₃. For *trans*-1,3-pentadiene the rate of hydrosilation is somewhat less than for 2-methyl-1,3-butadiene or 2,3-dimethyl-1,3-butadiene, and additionally, the major 1,4-hydrosilation product has the silyl group in the terminal position. The methyl group effect is almost certainly due to steric restrictions as the electronic effect is seemingly small in comparison to the electronic variation among the silanes investigated.

Acknowledgment. We thank the National Science Foundation and the Office of Naval Research for the support of this research. We also acknowledge the assistance of Mr. Steven Simoni.

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(9) Fellow of the Alfred P. Sloan Foundation 1974-1976.

Mark S. Wrighton,*⁹ Mark A. Schroeder

Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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A New Route to Highly Substituted 1,3-Disila- and -Digermacyclobutanes. The First 1,3-Distannacyclobutane

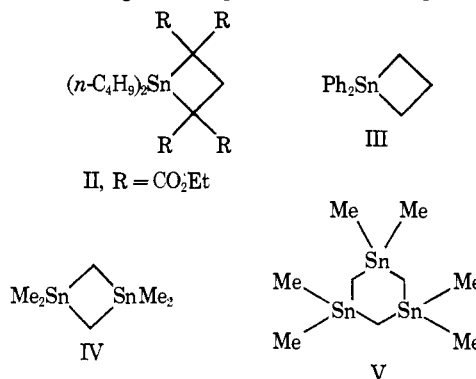
Sir:

The smallest characterized and fully documented cyclic system containing only tin and carbon atoms as ring members is I.^{1,2} Although various reports of



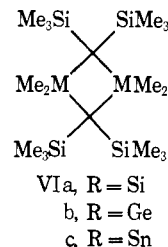
(1) H. Zimmer, C. W. Blewett, and A. Brakas, *Tetrahedron Lett.*, **1615** (1968).

SnC₃ and Sn₂C₂ ring systems have been published, satisfactory experimental evidence to support these claims is lacking. Compound II is in a patent claim³



and remains questionable and unsubstantiated; III has been listed in a review,⁴ but details concerning its preparation and structural characterization have not been forthcoming. Compound IV was claimed in a thesis,⁵ but further scrutiny of its reported method of preparation has shown that the smallest stannacyclobutane formed is the six-membered ring compound V.⁶

We report here a reaction which leads to the formation of 1,3-dimetallacyclobutanes of type VI in fair



yields. Noteworthy is the preparation of VIc, the first bonafide 1,3-distannacyclobutane.

The entry into this novel series of compounds was provided by our continued study of the lithium reagent (Me₃Si)₂CBrLi.⁷ This reagent, prepared by simultaneous addition of equimolar quantities of *n*-butyllithium in hexane and (Me₃Si)₂CBr₂ in THF, with stirring and under nitrogen, to dimethyl ether at -115°, was treated with 0.5 molar equiv of dimethyltin dichloride. After a reaction time of 90 min at -115°, the mixture was warmed to room temperature. (The orange color of the lithium reagent was discharged when the Me₃SnCl₂ was added, giving a light yellow solution which was colorless at room temperature.) Work-up of the pentane extract of the nonvolatile reaction residue by crystallization and column chromatography gave one major product, 1,1,3,3-tetramethyl-2,2,4,4-tetrakis(trimethylsilyl)-1,3-distannacyclobutane in 20% yield, based on the (Me₃Si)₂CBr₂ charged, mp 248-250° (sealed capillary). *Anal.* Calcd for C₁₈H₄₈Si₄Sn₂: C, 35.19; H, 7.87; mol wt, 614.3. Found:

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