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 HSiEt$_3$ using (C$_6$H$_6$)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 H$_2$ or D$_2$[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 (C$_6$H$_6$)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 readily[1] but no reaction could be detected with HSiEt$_3$. 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.

(7) (a) E. N. Frankel, *J. Org. Chem.*, **37**, 1549 (1972); (b) E. N. Frankel and R. O. Butterfield, *ibid.*, **34**, 3930 (1969); (c) E. N. Frankel and F. L. Little, *J. Amer. Oil Chem. Soc.*, **46**, 256 (1969); (d) M. Cais E. N. Frankel, and R. A. Rejoan, *Tetrahedron Lett.*, 1919 (1968).
(8) J. Nasielski, P. Kirsch, and L. Wilputte-Steinert, *J. Organometal. Chem.*, **27**, C13 (1971).
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Mark S. Wrighton,*[9] Mark A. Schroeder
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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

R$_2$Sn⟨▷⟩

I

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

SnC$_3$ and Sn$_2$C$_2$ ring systems have been published, satisfactory experimental evidence to support these claims is lacking. Compound II is in a patent claim[3]

II, R = CO$_2$Et

III

IV

V
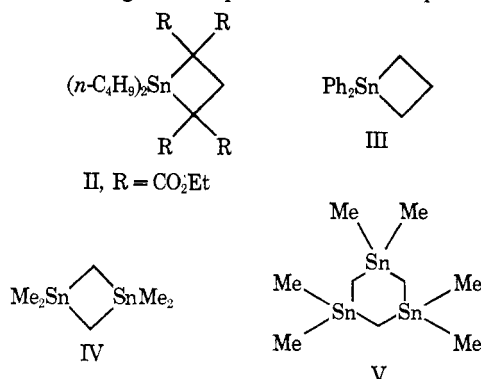
and remains questionable and unsubstantiated; III has been listed in a review,[4] but details concerning its preparation and structural characterization have not been forthcoming. Compound IV was claimed in a thesis,[5] but further scrutiny of its reported method of preparation has shown that the smallest stannacarbocycle 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

VIa, R = Si
b, R = Ge
c, R = Sn
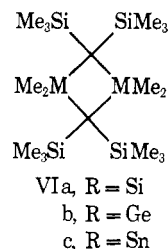
yields. Noteworthy is the preparation of VIc, the first bonafide 1,3-distannacyclobutane.

The entry into this novel series of compounds was provided by our continued study of the lithium reagent (Me$_3$Si)$_2$CBrLi.[7] This reagent, prepared by simultaneous addition of equimolar quantities of *n*-butyllithium in hexane and (Me$_3$Si)$_2$CBr$_2$ 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 Me$_2$SnCl$_2$ 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 (Me$_3$Si)$_2$CBr$_2$ charged, mp 248–250° (sealed capillary). *Anal.* Calcd for C$_{18}$H$_{48}$Si$_4$Sn$_2$: C, 35.19; H, 7.87; mol wt, 614.3. Found:

(2) For a recent review dealing with stannacycloalkanes see B. C. Pant, *J. Organometal. Chem.*, **66**, 321 (1974).
(3) G. P. Mack and E. Parker, U. S. Patent 2,604,483 (1952); *Chem. Abstr.*, **47**, 4358g (1953).
(4) M. Gielen, *Ind. Chim. Belge*, **38**, 20, 138 (1973).
(5) G. Berkowitz, Ph.D. Thesis, University of Pennsylvania, 1968; *Diss. Abstr. B*, **29**, 2334 (1969).
(6) (a) A. A. Buyakov, T. K. Gar, and V. F. Mironov, *Zh. Obshch. Khim.*, **43**, 801 (1973); (b) D. Seyferth and S. C. Vick, report in preparation.
(7) D. Seyferth, R. L. Lambert, Jr., and E. M. Hanson, *J. Organometal. Chem.*, **24**, 647 (1970).

C, 35.26; H, 7.88; mol wt, 636 (vpo in $CHCl_3$). Its mass spectrum (70 eV) showed, *inter alia*, the $(M - 15)^+$ and the $(M/2)^+$ fragment ions, but no evidence for species higher than $(M - 15)^+$ (up to m/e 900). The nmr spectrum (CCl_4) showed a singlet at δ 0.57 for the CH_3–Sn protons ($J(^{117}Sn-^1H)$ 45.5; $J(^{119}Sn-^1H)$ 48 Hz) and a singlet at δ 0.18 ppm (Me_3Si protons). Two other solid products present in trace yield were identified tentatively on the basis of their spectral properties as $Me_2Sn[CBr(SiMe_3)_2]_2$ and $(Me_3Si)_2C(SnClMe_2)_2$. The volatile components of the reaction mixture were identified as $(Me_3Si)_2CHBr$[7] (15% yield), $(Me_3Si)_2CBr_2$ (15%), and $n\text{-}C_4H_9CBr(SiMe_3)_2$[7] (30% yield). The yields of organotin products have not been optimized and reflect in part losses incurred in the purification procedures used.

Chemical evidence for the structure of the 1,3-distannacyclobutane product is provided by its reaction with an equimolar quantity of methyllithium at room temperature, followed by treatment of the resulting yellow solution with saturated aqueous NH_4Cl. The two products obtained, $(Me_3Si)_2(Me_3Sn)CH$ (bp 53–55° (10.4 mm), $n^{25}D$ 1.4881, 20% yield) and $Me_3SnC(SiMe_3)_2SnMe_2C(SiMe_3)_2H$ (VII) (mp 165–166°, 37% yield), must have been produced by hydrolysis of $(Me_3Si)_2(Me_3Sn)CLi$ and $Me_3Sn(Me_3Si)_2CSnMe_2C(SiMe_3)_2Li$, which are the expected cleavage products from the reaction of MeLi with VIc. The nmr spectrum of VII showed the five singlets expected for this structure at (in the order of the formula as written) δ 0.30, 0.23, 0.41, 0.18, and −0.15 ppm, with appropriate tin satellites for the $(CH_3)_nSn$ signals.

The action of 2 molar equiv of bromine in methanol at reflux on VIc resulted in only partial methyl group cleavage from tin, giving VIII (mp 261–265°) in 30%

VIII
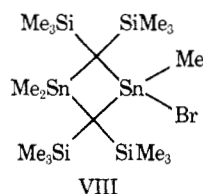
yield (together with a 62% recovery of VIc), rather than in endocyclic Sn–C cleavage. Although the latter process would be expected to be preferred in such a strained ring system, the steric hindrance introduced by the trimethylsilyl groups apparently prevents attack of the reagent at a ring carbon atom.

Similar reactions of $(Me_3Si)_2CBrLi$ (2 molar equiv) with dimethyldichlorosilane and with dimethyldibromogermane have given VIa (mp 208–210°, vpo mol wt 427 *vs.* 433 calcd, M^+ and $(M/2)^+$ species in the 70 eV mass spectrum, 36% yield) and VIb (mp 225–226°, vpo mol wt 503 *vs.* 522 calcd, M^+ and $(M/2)^+$ in the mass spectrum, 17% yield). In both reactions another type of product was isolated in low yield: $(Me_3Si)_2C(SiClMe_2)_2$ (mp >360°) in the case of the Me_2SiCl_2 reaction and $(Me_3Si)_2C(GeBrMe_2)_2$ (mp >360°) in the Me_2GeBr_2 reaction.

It is of interest to consider possible mechanisms which lead to these 1,3-dimetallacyclobutanes since their formation was unexpected and the competing and sequential reactions which take place when the Me_2MX_2 compounds are added to $(Me_3Si)_2CBrLi$ are by no

Scheme I[a]

[a] $R = (Me_3Si)$.

means straightforward. Scheme I shows an organolithium route which can account for all of the products isolated. The formation of IX, X, and XI as postulated is at first surprising, and these species are rather unusual. However, it must be remembered that these reactions are carried out at very low temperatures, at which Si–Cl, Ge–Br, and (less so) Sn–Cl bonds have a much diminished reactivity toward nucleophilic attack by organolithium reagents, but at which lithium–halogen exchange still is quite facile.[8] A special driving force which also will favor the formation of IX, X, and XI is the high stability of α-trimethylsilylalkyllithium reagents, which increases the more α-silyl groups are present.[9] The isolation of minor products of type $(Me_3Si)_2C(MXMe_2)_2$ does not necessarily indicate that IX is a precursor of VI, but if IX indeed is an intermediate, an additional route to VI involving elimination of LiX from IX to give $(Me_3Si)_2C=MMe_2$ and dimerization of the latter can be considered. This route we consider less likely than a process which proceeds entirely *via* organolithium intermediates.

Further extensions of this new 1,3-dimetallacyclobutane synthesis using other R_2MX_2 compounds and other organolithium reagents are in progress.

(8) *E.g.*, A. E. Bey and D. R. Weyenberg, *J. Org. Chem.*, **31**, 2036 (1966).
(9) M. A. Cook, C. Eaborn, A. E. Jukes, and D. R. M. Walton, *J. Organometal. Chem.*, **24**, 529 (1970).

Dietmar Seyferth,* James L. Lefferts
*Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139*