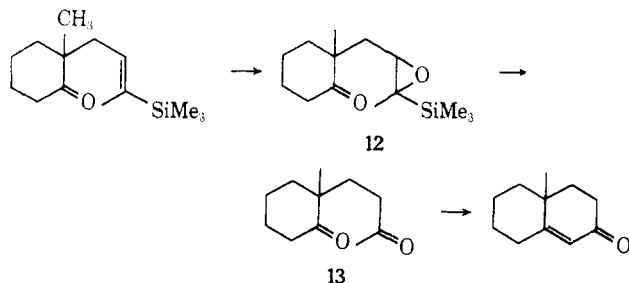11

unaffected by formic acid at room temperature or by heating with acetic acid in ethanol.
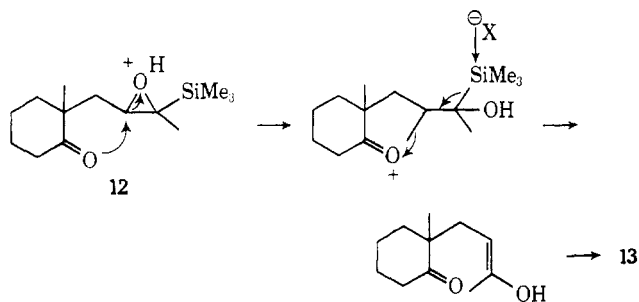
In startling contrast, while treatment of the ketonic vinylsilane **5** in methylene chloride with a slight excess of *m*-chloroperbenzoic acid at 0° for 10 min gives largely the epoxysilane **12**, further keeping of the re-

12

13

action mixture for 4 hr at room temperature led, in 90% yield, to the known dione **13**,[10] cyclized under the usual basic conditions to the octalone, identical with an authentic sample.

The transformation of the epoxysilane **12** to the dione **13** is evidently brought about merely by the *m*-chlorobenzoic acid formed in the epoxidation. Isolated epoxide **12** is also tranformed into **13** by shaking with formic acid for 30 sec (contrast the stability of **11** under these conditions).

We believe that the extreme ease of the transformation epoxysilane → ketone in this and similar cases (*vide infra*) strongly suggest nucleophilic participation of the carbonyl group in the epoxide opening, in a manner reminiscent of the carbonyl participation involved in the directed hydration of certain ketoacetylenes to 1,4- and 1,5-diketones.[11] A related mechanism is outlined for the **12** → **13** transformation.
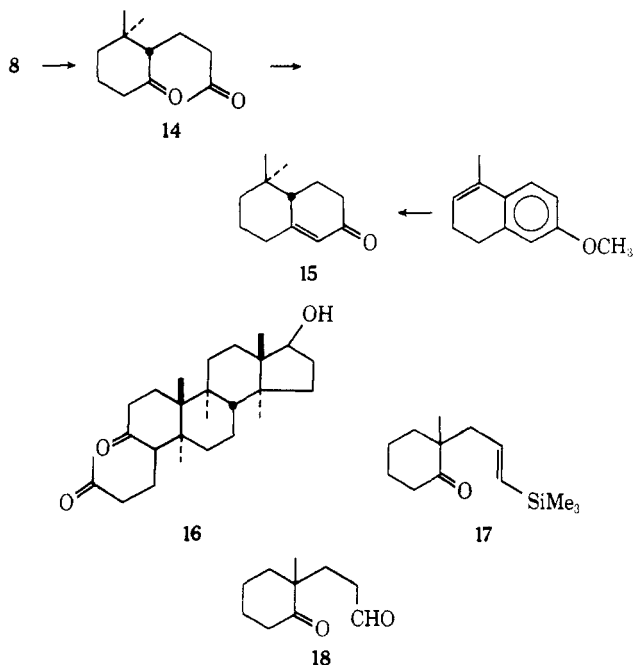
12

→ **13**

Under similar conditions, the vinylsilane **8** was transformed (final treatment with formic acid) to the dione **14** (83% yield), further cyclized in 82% yield (3 *M* potassium hydroxide in ethanol) to 5-methyl-Δ[1,9]-2-octalone (**15**) identical with an authentic sample made by Birch reduction of the known[12] 5-methyl-2-methoxy-7,8-dihydronaphthalene. The vinylsilane **7** was similarly converted in 71% yield to the corresponding dione **16**, mp 123–127°.
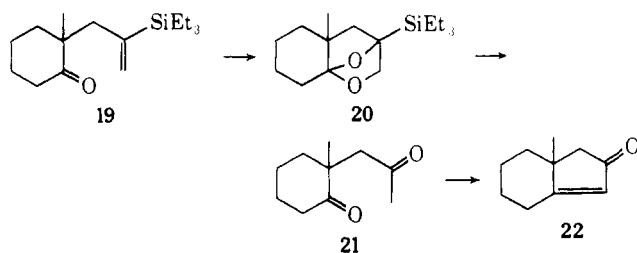
The cases described above all represent the use of a vinylsilane chain as a cyclohexenone precursor. The

(10) J. A. Marshall and D. J. Schaeffer, *J. Org. Chem.*, **30**, 3642 (1965).
(11) G. Stork and R. Borch, *J. Amer. Chem. Soc.*, **86**, 935 (1964). See also Y. Gaoni, *J. Chem. Soc.*, 2925, 2934 (1968).
(12) G. Stork, A. Meisels, and J. E. Davies, *J. Amer. Chem. Soc.*, **85**, 3419 (1963).

8 → **14**

15

16 **17**

18

method can, however, be used in other cases as well. For instance, the vinylsilane **17** (formed from the appropriate allylic iodide and **3**) gave after 29 hr at room temperature with *m*-chloroperbenzoic acid 60% yield of the aldehyde **18**, oxidized by Jones reagent to the corresponding keto acid.[13] Finally, the application to a cyclopentenone is illustrated by the conversion of the vinylsilane **19** (from **3** and the appropriate iodide). In

19 **20**

21 **22**

that case, the peracid treatment led not to the dione but, in agreement with the postulate of ketone participation, to the cyclic ketal **20** (quantitative yield). This, in keeping with the greater difficulty of eliminating the primary oxygen function, required refluxing with 20% sulfuric acid–methanol for quantitative conversion to the related dione **21**, cyclized (reflux with 1 *M* potassium hydroxide–methanol for 10 hr) in 83% yield to the known[14] methylhydrindenone (**22**).[15]

(13) R. L. Frank and R. C. Pierle, *J. Amer. Chem. Soc.*, **73**, 724 (1951).
(14) R. Fraisse-Jullien and C. Frejaville, *Bull. Soc. Chim. Fr.*, 4449 (1968).
(15) We thank the National Science Foundation and the National Institutes of Health for their support of this work.

Gilbert Stork,* **Michael E. Jung**
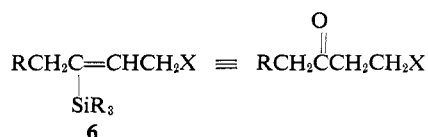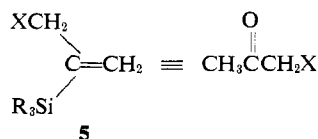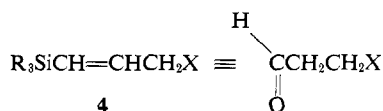*Department of Chemistry, Columbia University*
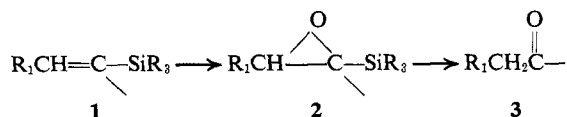*New York, New York 10027*

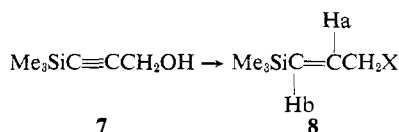## Synthetic Routes to Halomethyl Vinylsilanes

Sir:

The demonstration that the vinylsilane system can be used as a relatively unreactive masked carbonyl *via*

the transformation $1 \rightarrow 2 \rightarrow 3^1$ made it desirable to explore synthetic routes to alkylating agents embodying this function. The allylic halides of types **4**, **5**, and **6**

$$R_1CH{=}C{-}SiR_3 \longrightarrow R_1CH{-\!-}C{-}SiR_3 \longrightarrow R_1CH_2C{-}$$

1   **2**   **3**

$$R_3SiCH{=}CHCH_2X \equiv \overset{H}{\underset{O}{\underset{|}{C}}}CCH_2CH_2X$$

4

$$\underset{R_3Si}{\overset{XCH_2}{>}}C{=}CH_2 \equiv CH_3CCH_2X$$

5

$$RCH_2C{=}CHCH_2X \equiv RCH_2CCH_2CH_2X$$
$$\underset{SiR_3}{|}$$

6

appeared especially valuable in this connection. This communication records their synthesis, as well as a number of observations which are not without interest in furthering our understanding of the chemistry of functionally substituted organosilanes.

The synthesis of alcohols **4**, X = OH, was easily achieved by lithium aluminum hydride reduction, e.g., of the readily available 3-hydroxypropynyltrimethyl-silane (**7**)^2 to **8**, X = OH:^{3,4} nmr $\delta(CCl_4)$ 6.03 (1 H, d(J

$$Me_3SiC{\equiv}CCH_2OH \rightarrow Me_3SiC{=}\overset{Ha}{\underset{Hb}{C}}CH_2X$$

7   **8**

= 19 Hz) of t (J = 3 Hz), Ha) 5.85 (1 H d, J = 19 Hz, Hb) 4.02 (2 H, d, J = 3 Hz) 3.20 (1 H, b s) 0.03 (9 H, s), from which the related chloride (triphenylphosphine–carbon tetrachloride^5), and iodide, **8**, R = CH_3, X = I (from the chloride and sodium iodide in acetone, 5.5 hr at room temperature) were readily prepared.

Allylic bromination (N-bromosuccinimide–benzoyl peroxide in refluxing carbon tetrachloride) proved a simple route from the known isopropenyltriethylsilane^6 to **5**, R = C_2H_5, X = Br, and the corresponding iodide **5**, R = C_2H_5, X = I.

The synthesis of the 3-ketoalkyl equivalents of type **6** was a considerably more difficult problem. It was unfortunately found that allylic bromination of **9**^{7}

$$Et_3Si\diagdown H \quad \rightarrow \quad Et_3Si\diagdown H \quad + \quad Et_3Si\diagdown H$$
$$\underset{CH_3}{} \underset{CH_3}{} \quad \underset{CH_3}{} \underset{CH_2Br}{} \quad \underset{BrCH_2}{} \underset{CH_3}{}$$

9   **10**   **11**

$$CH_3C{\equiv}CCH_2OH \rightarrow CH_3C{=}\overset{Et_3Si\ H}{\underset{}{C}}CH_2OSiEt_3 + CH_3C{=}\overset{H\ SiEt_3}{\underset{}{C}}CH_2OSiEt_3$$

12   **12a**

with N-bromosuccinimide, which might have provided a simple route to **10**, actually gave both **10** and its isomer **11** in the ratio of 2:3.

Addition of triethylsilane to 3-butyn-1-ol in the presence of chloroplatinic acid gave a mixture of two regio-isomers **12** and **12a**, although the major product (not easily separable) was the desired **12**. The silylation of several derivatives of 3-butyn-1-ol in which the hydroxyl was variously protected did not lead to the desired β-addition to substances of type **12** but the potentially important observation was made that treatment of the trimethyl acetate **13** (bp 85–90° (28 mm)

13

3.1 g) with 1 equiv of triethylsilane and 0.5 ml of 10% aqueous chloroplatinic acid for 2 hr at 120° and 3 hr at 100° gave, in 83% yield, the regiospecifically formed **14** (bp 90° (0.5 mm)) which was converted (lithium aluminum hydride) to the alcohol **15** (bp 110–112° (9 mm), nmr (CCl_4) δ 1.76 (3 H, d, J = 7 Hz, CH_3) and 5.87 (1 H, q, J = 7 Hz, CH=C)). We ascribe this remarkable directional effect to coordination of a tri-alkylsilylplatinum hydride intermediate^8 to the carbonyl oxygen of the trimethylacetate group. *This should be a general entry into α-silylated homologs of allyl alcohol.*

Two methods can be used for the synthesis of the 3-ketobutyl precursor **6**, R = CH_3, X = I, as a mixture of Z and E isomers in which the former predominates.

The known 3-trimethylsilyl-2-butenol (**17**) could be

$$CH_3\overset{Cl}{\underset{}{C}}{=}CHCH_2Cl \rightrightarrows CH_3\overset{Cl}{\underset{}{C}}{=}CHCH_2OSiMe \rightrightarrows$$
                 16

$$CH_3\overset{SiMe_3}{\underset{}{C}}{=}CHCH_2OH \longleftarrow CH_3\overset{SiMe_3}{\underset{}{C}}{=}CHCHO$$
       17   **18**

made by minor modifications of the method of Petrov,^{9} using the Wurtz coupling of the trimethylsilyl ether **16** of 3-chloro-2-butenol with trimethylchlorosilane (sodium in boiling toluene, high speed stirring). The alcohol **17** resulting after acid hydrolysis of the silyl ether (aqueous fluoboric acid–ether) was then converted via the chloride to the iodide **6**, R = CH_3, X = I. The

(1) G. Stork and E. Colvin, *J. Amer. Chem. Soc.*, **93**, 2080 (1971); G. Stork and M. Jung, *ibid.*, **96**, 3682 (1974).

(2) V. F. Mironov and N. G. Maksimova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2059 (1960).
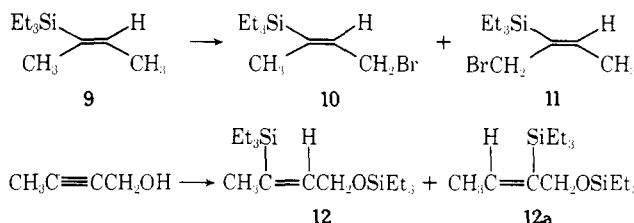
(3) It has been reported^2 that Pt-catalyzed addition of methyldiethyl-silane to propargyl alcohol takes place to produce the analog of **8**, X = OH. Our experience, using triethylsilane, produced nonregiospecific addition.

(4) Satisfactory nmr, ir, and mass spectral data were obtained for all new compounds reported. Chloroform (δ 7.24) was used as an internal standard for the nmr spectra of compounds containing the trimethylsilyl group.

(5) I. M. Downie, J. B. Holmes, and J. B. Lee, *Chem. Ind. (London)*, 900 (1966); J. Hooz and S. S. H. Gilani, *Can. J. Chem.*, **46**, 816 (1968).
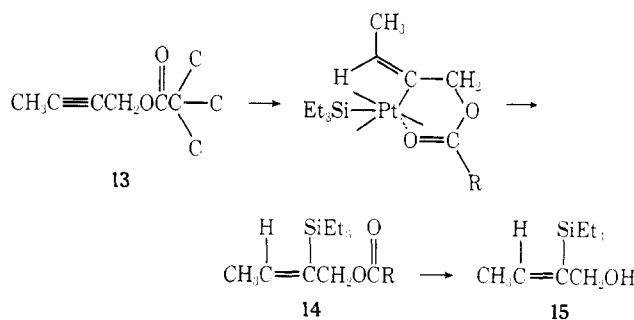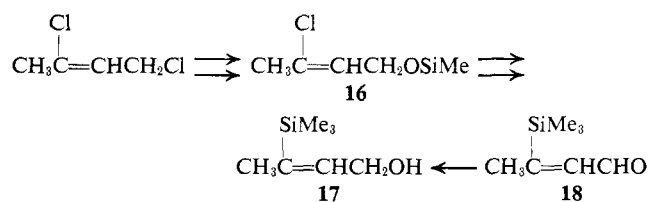
(6) A. D. Petrov and G. I. Nikishin, *Zh. Obshch. Khim.*, **26**, 1233 (1956).

(7) Made by the usual chloroplatinic acid-catalyzed addition of triethylsilane to 2-butyne (70% yield, bp 59–64° (2 mm)).
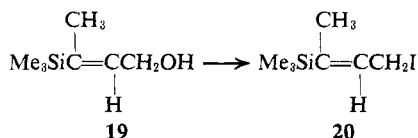
(8) For a discussion of the mechanism of platinum catalyzed silyla-tion, see A. J. Clark and J. F. Harrod, *J. Amer. Chem. Soc.*, **87**, 16 (1965).

(9) A. D. Petrov, V. F. Mironov and V. G. Glukhovtsev, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 461 (1956).

method suffers from the fact that the starting 3-chloro-2-butenol (from the hydrolysis of commercial 1,3-dichloro-2-butene, a mixture of Z and E isomers) is not stereochemically homogeneous. The final iodide is a 5 : 1 mixture of Z and E isomers.
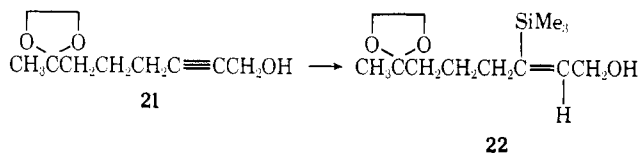
A similar mixture (Z/E 4 : 1) could be obtained more simply by sodium borohydride reduction of the unsaturated aldehyde 18[10] available in essentially two steps from propargyl tert-butyl ether.

The pure E isomer of 17 could be made by applying Corey's method[11] to the readily available trimethylsilylpropargyl alcohol 7.[2] Reduction with lithium aluminum hydride, followed by trapping with iodine at −78° and coupling of the pure Z iodo alcohol (bp 62° (0.08 mm)) with lithium dimethylcuprate gave in 70% yield from 7 the pure E isomer 19 (bp 85–87°

(9 mm)): nmr δ (CCl₄) 5.80 (1 H, t, $J = 6$ Hz of q, $J = 1$ Hz, HC=C) 1.71 (3 H, d, $J = 1$ Hz, CH₃). The alcohol was converted to the chloride (triphenylphosphine–carbon tetrachloride, 60% yield, bp 55–56° (12 mm)) which then gave the E iodide 20 (sodium iodide–2-butanone, 50°, 1 hr, evaporative distillation at 60° (20 mm)) in 80% yield.

The instability of some cuprates makes this method unsatisfactory for the synthesis of certain homologs of 6 in which R ≠ H. After many attempts, the most general route to homologs was found to involve introduction of the silane function as the last step in the synthesis, as illustrated for the synthesis of 22. Alkyla-

tion of the dianion of propargyl alcohol (2 equiv of lithium amide in liquid ammonia–tetrahydrofuran) with the dioxolane of iodopropyl methyl ketone gave a 90% yield of 21, bp 99–107° (0.1 mm). Reduction and iodination (as in 17 to 18) then gave the crude Z iodo alcohol. Silylation of the hydroxyl group (hexamethyldisilazane–trimethylchlorosilane–pyridine) coupling with trimethylchlorosilane (as in 14 to 15) and hydrolysis of the silyl ether (5% potassium carbonate in 30% aqueous methanol, 42 hr, room temperature) gave, in 41% overall yield from propargyl alcohol, the silylated allylic alcohol 22 (6, R = CH₃C(O)₂CH₂-CH₂H₂, X = OH) which should be useful for bis-annelation reactions by the vinylsilane method.[12]

(10) R. Mantione and Y. Leroux, J. Organometal. Chem., 31, 5 (1971).
(11) E. J. Corey, J. A. Katzenellenbogen, N. W. Gilman, S. A. Roman, and B. W. Erickson, J. Amer. Chem. Soc., 90, 5618 (1968).
(12) We thank the National Science Foundation and the National Institutes of Health for their support of this work.

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Reactions of LiCuHR. Selective Removal of Halo and Mesyloxy Groups and Reduction of α,β-Unsaturated Ketones

Sir:

We wish to outline the scope and limitation of reactions utilizing Cu(I) complexes which can be conventionally represented by LiCuHR (R = alkyl and alkynyl). These mixed ate complexes achieve two operations, (i) reductive removal of halo and mesyloxy groups and (ii) conversion of α,β-unsaturated ketones to the corresponding saturated compounds, and are evaluated in terms of reagent-to-substrate ratio, structure of R, solvent effect, temperature, and substrate. Of special significance is the superb selectivity of the newer reagents, compared to one [2LiAlH(OCH₃)₃ + CuI] previously reported,[1] and, moreover, invariable ligand transfer of hydrogen rather than the R group in all cases examined attracts mechanistic interest.[2] For instance, LiCuH(n-C₄H₉) converts ethyl 12-mesyloxystearate almost quantitatively into ethyl stearate within 2 hr at 25°, and cyclohex-3-enyl mesylate provides cyclohexene without a detectable amount of cyclohexadiene. A summary of results is given below.

There are several methods to prepare CuH.[3] The Whitesides procedure[3c] is adopted and is used throughout this work.[4,5] An equimolar amount of LiR was added to a stirred suspension of CuH either in ether or tetrahydrofuran maintained at −40°.[6,7]

Removal of Halo and Mesyloxy Groups.[1,8] Using 2-bromononane, we have examined reaction variables that influence the reactivity of the ate complexes and the yield of product (n-nonane contaminated with a minute amount (3–4%) of n-nonene). Table I entries 1–4 show that 4 molar equiv of the cuprate is required to complete the reduction within a short reaction time. Of several complexes differing in R, the reaction pro-

(1) S. Masamune, P. A. Rossy, and G. S. Bates, J. Amer. Chem. Soc., 95, 6452 (1973).
(2) In the absence of accurate rate data, we cannot exclude the (remote) possibility of disproportionation (2LiCuHR ⇌ LiCuH₂ + LiCuR₂) although such a reaction has not been confirmed for the cuprate species. See (a) H. O. House, D. G. Koespell, and W. J. Campbell, J. Org. Chem., 37, 1003 (1972); (b) G. H. Posner, C. E. Whitten, and J. J. Sterling, J. Amer. Chem. Soc., 95, 7788 (1973). For approximate reaction rates of LiCu(n-C₄H₉)₂, see, e.g., (c) G. M. Whitesides, W. F. Fischer, Jr., J. S. Filippo, Jr., R. W. Bashe, and H. O. House, ibid., 91, 4871 (1969); (d) E. J. Corey and G. H. Posner, ibid., 90, 5615 (1968).
(3) (a) E. Wiberg and W. Henle, Z. Naturforsch. B, 7, 250 (1952); (b) J. A. Dilts and D. F. Shriver, J. Amer. Chem. Soc., 90, 5769 (1968); 91, 4088 (1969); (c) G. M. Whitesides, J. S. Filippo, Jr., E. R. Stredronsky, and C. P. Casey, ibid., 91, 6542 (1969); G. M. Whitesides and J. S. Filippo, Jr., ibid., 92, 6611 (1970); (d) S. A. Bezman, M. R. Churchill, J. A. Osborn, and J. Wormald, ibid., 93, 2063 (1971); (e) M. A. Kazankova, I. G. Malykhina, M. B. Terenina, and I. F. Lutsenko, J. Gen. Chem. USSR, 42, 2129 (1972).
(4) The ate complex derived from CuH that is prepared from CuBr and (C₂H₅)₃SnH³ᵉ resulted in poor yields of reduction products for reasons as yet unknown to us.
(5) Although reductive removal of some halides with CuH was previously noted (ref 3c), we found that 1-bromononane was virtually unaffected with CuH in either ether or THF at −40° for 12 hr, conditions under which the reduction was complete with most of the ate complexes.
(6) An alkynyl lithium solution was prepared from the alkyne and halide-free methyl lithium available from the Foote Mineral Co. H. O. House and W. F. Fischer, Jr., J. Org. Chem., 33, 949 (1968).
(7) The 1 : 1 ratio of CuH/RLi should be accurately followed. An excess of either reagent greatly decreases the yield of products. CuH is uniformly brown (light to dark) and any mottling or separation of pale yellow solid (presumably CuI) should not be observed.
(8) Other methods are (a) R. O. Hutchins, B. E. Maryanoff, and C. A. Milewski, Chem. Commun., 1097 (1971); (b) C. W. Jefford, D. Kirkpatrick, and F. Delay, J. Amer. Chem. Soc., 94, 8905 (1972); (c) H. C. Brown and S. Krishnamurthy, ibid., 95, 1669 (1973); (d) R. E. Ireland, D. C. Muchmore, and U. Hengartner, ibid., 94, 5098 (1972).