methylsilyl)methyl trifluoromethanesulfonate (21.2 mmol) in ether (15 mL) was added. Immediate, complete reaction to give a single product was indicated by gas chromatographic analysis of a worked-up sample. The cold reaction mixture was poured into H_2O (100 mL) and extracted with ether (4 × 50 mL) to give 90% of 1-(trimethylsilyl)-2-nonyne as determined by gas chromatographic comparison with a standard solution. Distillation gave 3.24 g (78%): bp 69–70 °C, (1.9 torr); ^{1}H NMR δ 0.09 [$(CH_3)_3Si$], 2.02 ($RCH_2C{\equiv}C$); ^{13}C NMR δ -2.06 [$(CH_3)_3Si$], 7.03 (CH_2Si), 77.25 and 78.92 ($C{\equiv}C$). The ^{13}C NMR spectrum showed only one component to be present (>97%). Anal. Calcd for $C_{12}H_{24}Si$: C, 73.38; H, 12.32. Found: C, 72.96; H, 12.15.

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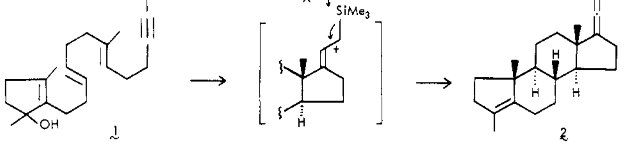
Propargylsilane Function as a Terminator of Biomimetic Polyene Cyclizations Leading to Steroids[1,2]

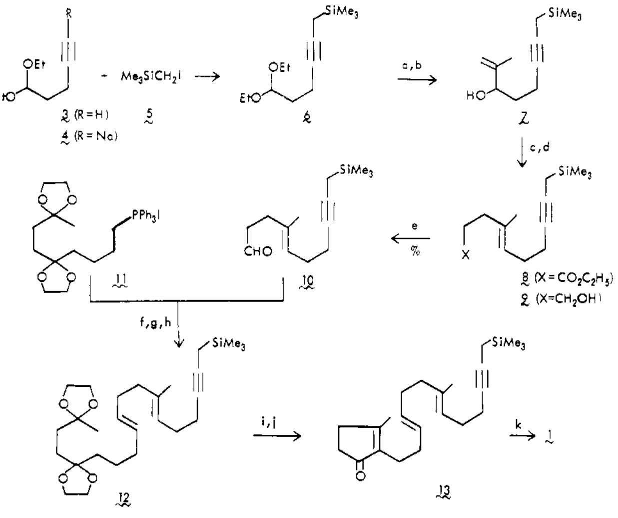
Sir:

The recent discovery that the allylsilane residue can serve as an efficient function for terminating biomimetic polyene cyclizations[3] has prompted us to examine the related system in which the allylsilane is replaced by the propargylsilane moiety. This latter function, when positioned as in formula **1**, has the potential of participating in a cyclization so as to produce a steroidlike tetracyclic substance (**2**) having a vinylidene substituent at C-17.[4] This structure is particularly intriguing because an allene group of this type can be converted, in a *single step* (via exhaustive hydroxylation), into the complete cortical side chain.[5] Accordingly, we undertook a study of the synthesis and cyclization of the substrate **1**, which is the subject of the present communication.



The synthesis of **1** was performed by a convergent scheme (Scheme I), the key step being the Wittig–Schlosser condensation of the known phosphonium salt **11**[6] with the aldehyde **10**. Scheme I is analogous to the one already described in detail for the preparation of the de(trimethylsilyl) substrate (**1** with H in place of Me_3Si).[6]

Scheme I



[a] To give the aldehyde: 5:1 THF/10% HCl, 27 °C, 2 h. [b] 2.8 mol equiv of $CH_2{=}C(CH_3)MgBr$, THF, -5 °C, 1.5 h. [c] To give 8: 11.6 mol equiv of $CH_3C(OEt)_3$, 0.2% $C_2H_5CO_2H$, 130 °C, 40 min. [d] To give 9: 1.5 mol equiv of $LiAlH_4$, THF, 0 °C, 3 h. [e] 2.3 mol equiv of $(C_5H_5NH)_2Cr_2O_7$, CH_2Cl_2, 22 °C, 24 h. [f] 11 + 0.82 mol equiv of C_6H_5Li, THF, 0 °C, 15 min. [g] 0.68 mol equiv of **10**, -78 °C, 1 h. [h] 0.89 mol equiv of C_6H_5Li, Et_2O, -78 °C then 0 °C, 10 min. [i] To give the diketone: 1:3 10% HCl/THF, 22 °C, 24 h. [j] 8:12:72 THF/MeOH/10% NaOH, 48 h, 22 °C. [k] Excess MeLi, Et_2O, 0 °C (four treatments).

The acetylenic acetal **3**,[7] prepared by reaction of commercially available 1,1-diethoxy-3-chloropropane with lithium acetylide, was converted into the sodio derivative **4** with 1.9 mol equiv of sodium amide. It was necessary to remove all of the ammonia and to perform the alkylation with 1.2 mol equiv of (iodomethyl)trimethylsilane[8] in THF (22 °C, 21 h); otherwise the product **6** was contaminated with the isomer resulting from rearrangement of the acetylenic bond from the β,γ to the α,β position. The acetal **6**,[9d,10] which was obtained in 42% yield, was hydrolyzed to the aldehyde[9d,10] (77% yield) and then treated with isopropenylmagnesium bromide to give the allylic alcohol **7**,[10] which was simply filtered through Celite (98% yield) before use in the next step. The orthoacetate Claisen reaction[11] with **7** gave the ester **8**[9d,10] (75% yield), which on hydride reduction afforded the corresponding alcohol **9**[9a,10] (89% yield). Finally, oxidation with pyridinium dichromate[12] gave the aldehyde **10**[9a,10] in 71% yield.

The Wittig–Schlosser condensation of **10** with **11** was performed by a procedure similar to one previously described;[6] however, it was necessary to avoid the use of excess phenyllithium; otherwise there was some isomerization of the acetylenic to an allenic bond. The product **12**[9b,10] was produced in 71% yield, and the *E*/*Z* ratio of the pro-C-8,9 olefinic bond was 96:4 as determined by GC analysis of the enone **13** derived therefrom (see below). Deketalization of **12** followed by cyclodehydration of the resulting dione[9a,10] afforded the enone **13**[9a,10] in 45% yield. It was necessary to use especially mild conditions for these last two steps in order

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(1) For a recent paper in the series on biomimetic cyclization, see: Gravestock, M. B.; Morton, D. R.; Boots, S. G.; Johnson, W. S. *J. Am. Chem. Soc.* **1980**, *102*, 800.

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(4) (a) Note that A. D. Despo and P. E. Peterson have reported that the solvolysis of 8-(trimethylsilyl)-6-octyn-2-yl tosylate affords 2-vinylidene-1-methylcyclopentane, 179th National Meeting of the American Chemical Society, Houston, Texas, March 24–28, 1980; Despo, A. D.; Chiu, S. K.; Flood, T.; Peterson, P. E. *J. Am. Chem. Soc.* preceding paper in this issue. (b) For examples of intermolecular reactions of propargylsilanes with electrophiles, see: Bourgeois, P.; Mérault, G. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1971**, *273*, 714; *J. Organomet. Chem.* **1972**, *39*, C44. Deleris, G.; Dunogues, J.; Calas, R. *Ibid.* **1975**, *93*, 43.

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(9) The product was purified by (a) chromatography on Florisil, (b) chromatography on alumina, (c) chromatography on silica gel, and (d) distillation at reduced pressure through a short-path apparatus, or a short Vigreux column, or (for high-boiling compounds and/or small amounts of material) a Kugelrohr with a Büchi Kugelrohrofen.

(10) (a) The NMR and IR spectra were consistent with the assigned structures. (b) A satisfactory combustion analysis was obtained for this compound.

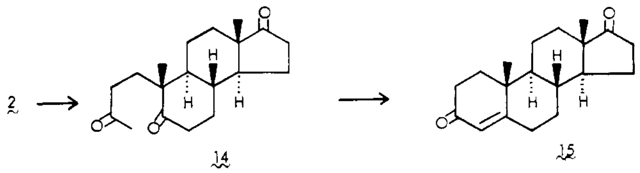
(11) Johnson, W. S.; Brocksom, T. J.; Loew, P.; Rich, D. H.; Werthemann, L.; Arnold, R. A.; Li, T.-t.; Faulkner, D. J. *J. Am. Chem. Soc.* **1970**, *92*, 4463.

(12) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399.

to minimize the formation of impurities showing short retention time peaks in the GC analysis, probably resulting from desilylation. The yield of **13** is probably subject to considerable improvement. Finally, treatment of the enone **13** with methyllithium yielded the substrate **1** which, because of its sensitivity, was used without purification for the cyclization studies.

Addition of the substrate **1** to a 0.5% solution of trifluoroacetic acid in dichloromethane maintained at −35 °C for 1 h produced a crystalline hydrocarbon fraction, isolated[9a] in 58% yield, containing two components in a ratio of 88:12 as shown by GC analysis. Pure crystalline specimens of these two hydrocarbons were obtained by preparative GC. The major component was assigned the structure **2** on the basis of chemical conversions (see below) and its spectral properties: mass spectra 282 (M^+, 25%), 91 (100%); IR 1965 cm^{-1}; NMR 4.68 (m, 2 H at C-21), 1.57 (s, vinylic CH_3), 0.91 and 0.88 ppm (2 s, angular CH_3). The minor component showed very similar spectral properties and was clearly an isomeric allenic compound which is presumed, by analogy to previous work,[13] to be the 13α epimer of **2** with a C/D cis ring fusion.

Unequivocal proof for structure **2** was afforded by ozonolysis [in CH_2Cl_2, pyridine, −70 °C, with reductive (Zn + HOAc) processing] of the mixture of tetracyclic hydrocarbons which gave the triketone **14** contaminated with some of the presumed 13α epimer. This product on cyclodehydration (2% NaOH/ethanol/THF 4:2:5, 25 °C, 4 h) afforded in 55% overall yield the enedione **15** contaminated with 12% (by GC) of the presumed 13α epimer. Purification[9b] readily afforded a 46% yield of *dl*-**15**, mp 127–130 °C (reported[6] 128–130 °C), which had NMR, solution IR, GC, and TLC properties that were identical with those of authentic (naturally derived) 4-androstene-3,17-dione.



Thus, the cyclization **1** → **2** has been realized in a yield that is most promising, considering that it has not been optimized; indeed, only one set of reaction conditions have been examined as yet. The removal of the presumed 13α epimeric contaminent promises to be easily accomplished by chromatography, particularly after oxygen atoms have been introduced into the molecule as shown above as well as in other examples.[13] We now look forward to examining the asymmetric cyclization of a modified form of the substrate **1** having an OH at pro-C-11[14] as well as to utilizing the allenic function for developing the cortical side chain.[5]

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[14] See: Johnson, W. S.; Brinkmeyer, R. S.; Kapoor, V. M.; Yarnell, T. M. *J. Am. Chem. Soc.* **1977**, *99*, 8341, including previous articles.

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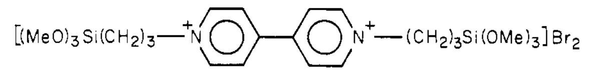
Thermodynamically Uphill Reduction of a Surface-Confined *N,N′*-Dialkyl-4,4′-bipyridinium Derivative on Illuminated p-Type Silicon Surfaces

Sir:

We wish to report the first results pertaining to a chemically derivatized p-type semiconductor photocathode surface. While p-type semiconductor electrodes do not suffer the gross decomposition typically found for their n-type counterparts,[1-3] kinetics for photocathodic H_2 evolution and surface instability are important problems that may be solved by surface modification.[4,5] Promising results for stabilizing n-type semiconductors with respect to photoanodic corrosion have previously been reported with ferrocene-centered surface modifiers.[6] Our new efforts concern the study of a p-type surface-confined *N,N′*-dialkyl-4,4′-bipyridinium derivative, since we previously showed that solution-dissolved *N,N′*-dimethyl-4,4′-bipyridinium could be photoreduced in an uphill sense at illuminated p-type Si.[4] Further, the reduced form of *N,N′*-dimethyl-4,4′-bipyridinium comes into rapid redox equilibrium with aqueous (pH <6) solutions containing suspensions of Pt to evolve H_2;[7] the H_2 evolution can also be catalyzed by hydrogenase.[8] We include results for derivatized Pt to establish the thermodynamics for the surface-confined reagent. We note possible applications in bioelectrochemistry and in electrochromic displays with reversible electrodes functionalized with the bipyridinium reagent.[9]

The surface-derivatizing agent, I, was prepared by refluxing dry 4,4′-bipyridine (Aldrich Chemical Co.) with 1-bromo-3-trimethoxysilylpropane [prepared by reacting $HC(OMe)_3$ with 1-bromo-3-trichlorosilylpropane purchased from Petrarch Chemical Co.] in rigorously dry CH_3CN solution. Reagent I was isolated as a pale yellow solid bromide salt by crystallization from CH_3CN solution by adding Et_2O.[10] UV–vis and ^1H NMR spectroscopy accords well with the structure shown, and redox behavior is consistent with isolation of a derivative of *N,N′*-dialkyl-4,4′-bipyridinium with $E°$ values of ∼−0.5 and −0.9 V vs. SCE for the first and second reversible, one-electron reductions in CH_3CN, respectively.[11]



I

The hydrolytically unstable $Si(OMe)_3$ groups provide a site for attachment to surfaces bearing OH groups, and in the presence of H_2O polymerization of I is possible.[12] Figure 1 shows a

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