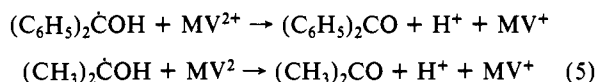


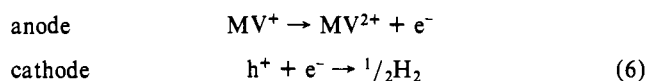
Figure 1. Plot of photocurrent with time for benzophenone/2-propanol/ MV^{2+} in the photoanode compartment. Solid line: current in the presence of MV^{2+} . Dashed line: current in the absence of MV^{2+} . Abscissa is photocurrent in μA ; ordinate is time in minutes.

described above does produce a small photocurrent; however, formation of the "normal" photoproduct, benzpinacol, is not entirely suppressed, indicating that oxidation of the ketyl radicals at the electrode is relatively inefficient compared to other processes. A striking increase in the efficiency of the photocurrent generated can be obtained by adding a small amount of methylviologen as a "mediator". MV^{2+} does not quench the benzophenone triplet efficiently, and under the reaction conditions, the quenching by MV^{2+} is negligible.¹⁹ However, it is expected that MV^{2+} should efficiently oxidize both ketyl radicals as indicated in eq 5.²⁰ The



2-hydroxy-2-propyl radical reacts with the substrate, MV^{2+} in this case, rather than transferring hydrogen to Ph_2CO to yield another Ph_2COH radical.²¹ Further, other studies have indicated that MV^{2+} can oxidize radical and diradical species generated in intra- and intermolecular hydrogen atom abstraction processes concurrent with transient or permanent formation of MV^+ .²²⁻²⁴

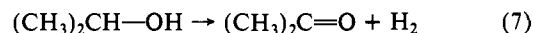
In the present studies, irradiation of benzophenone/2-propanol/ MV^{2+} solutions in the photoanode compartment (366-nm absorbed light, intensity 1.4×10^{-8} einstein/s) leads to a buildup of moderate levels of MV^+ and to a steady photocurrent of 320 μA (Figure 1). The MV^+ is oxidized at the anode of the photolyzed compartment with concomitant reduction of H^+ in the cathode compartment (1 M HCl). The two half-cell reactions are



There was no decrease in benzophenone concentration over moderate periods of irradiation, and a steady production of hydrogen in the cathode compartment was observed. No benzpinacol could be detected for irradiation times on the order of 1-2 h. In these experiments as with the RuL_3^{2+}/Et_3N system, the photocurrent produced was linear with the square of absorbed light intensity. The quantum efficiency at the above-indicated intensity

is 22%; quantitative analysis of the hydrogen produced gives good agreement with this value.

The overall reaction mediated by MV^{2+} in the photoelectrochemical cell is the oxidation of 2-propanol (eq 7). This reaction



is endothermic by 20 kcal/mol so that as carried out the reaction involves simultaneous generation of electricity and chemical conversion. Given the wide variety of photoinduced electron-transfer and hydrogen atom abstraction processes previously reported, it should be possible to greatly extend the scope of these studies. For example, since both ketones and N-heteroaromatics can abstract hydrogen atoms from alkanes, it should be possible to mediate net dehydrogenation of alkanes, a process endothermic by ca. 33 kcal. Although the present studies with benzophenone require excitation in the near-UV, preliminary studies with benzil and acridine indicate modest photocurrents can be obtained with these systems by using longer wavelength light. We are currently extending our studies to systems in which other reducing species or potential oxidants can be generated by excitation in the visible region.

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Propargylsilane and (Trimethylsilyl)alkyne Terminator Groups. Formation of an Exocyclic Allene in the Acetolysis of 8-(Trimethylsilyl)-6-octyn-2-yl Tosylate

Sir:

Triple-bond participation in reactions giving 6- and/or 5-membered rings was reported from our laboratories in 1966^{1a} and 1969.^{1b} Other related work appeared at approximately the same time.² More complex syntheses based on triple-bond cyclization have appeared.³ Johnson and co-workers utilized the propyne terminator in their spectacular olefinic-acetylenic cyclizations to give steroidlike products.⁴ For several reasons,^{4d} still better terminators are needed, and the search for them is being actively pursued.⁴

We have now studied the cyclization in acetic acid of the tosylate **1** containing the previously uninvestigated propargylsilane terminator and, for comparison, the cyclization of tosylate **5** in which a terminally silylated alkyne, recently used also by others,^{5,6} serves as the participating group (see Schemes I and II). The trimethylsilyl group present in **1** was expected to direct the cyclization toward 5-membered ring formation by β stabilization of the cationic transition state or intermediate **2**, which could lead to allene **4** or to cyclic vinylic acetates and products derived from them. The allylsilane group has played a comparable role in cyclizations reported in the literature,⁷ including a steroid-forming

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(19) We measure $kq = 1.03 \times 10^7 M^{-1} s^{-1}$ for quenching of the benzophenone triplet by MV^{2+} under these conditions (quenching of phosphorescence in degassed acetonitrile). Therefore, only about 1.3% of the triplets is quenched by MV^{2+} whereas the remainder reacts with 2-propanol.

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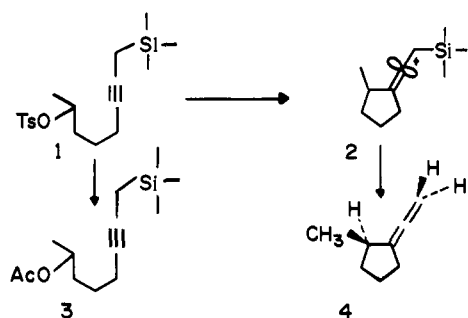
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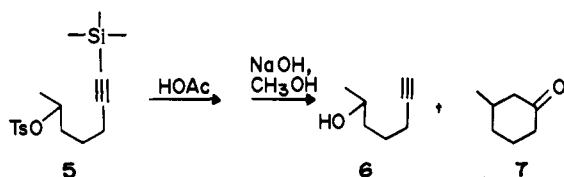
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Scheme I



Scheme II



cyclization,^{7c} and in numerous acyclic electrophilic reactions.⁸

In our study, the allene **4** was, in fact, formed along with the product of direct substitution, **3**, in the ratio **4**:**3** = 77:23. Compounds **4** and **3** accounted for 92% of the area in the gas chromatogram of the products. Four minor peaks (no more than 2.5% each) were detected. The ¹H NMR spectrum of gas chromatographic fraction **4** at 400 MHz showed a highly characteristic pattern, identical except for impurity peaks with the pattern of a reference sample synthesized from 2-methylcyclopentanone and CH₂=CBrSiMe₃.⁹ Carbon-13 NMR further substantiated structure **4**.

The terminally silylated alkyne tosylate **5** gave, after hydrolysis and cleavage of silicon (NaOH in MeOH), a mixture of the parent acyclic alcohol (**6**) (62%) and 3-methylcyclohexanone (**7**) (38%).

The percentages of cyclization determined in our study are summarized in Table I, along with the previously reported results^{1b} for the unsilylated analogues. We also determined the rates of reaction in order to assess the influence of the two types of silicon substituents upon the nucleophilicity of the triple bond. Quantitative data in this area are sorely lacking, since most of the work has been synthetic. Our rate results are also given in Table I.

A generalization of our results is that the cyclic products are those which would be expected on the basis of β-cation stabilization by silicon but that the transition states (rates) reflect the β stabilization only to a small extent. The moderately increased rates of cyclization do lead to small increases in the percent of cyclization (Table I). The relatively clean formation of the exocyclic allene **4** is in marked contrast with the zero yield obtained¹⁰ in an attempt to achieve the addition of cations to propargylsilane under reaction conditions which succeed in the case of allylsilanes. The formation of a single cyclic product (allene) is strikingly advantageous in the identification of the reaction products. The previously used terminator group, CH₃C≡C-,^{1b} led to substantial amounts of four isomers (cis and trans isomers having ring sizes five and six) although the steroidal cyclization⁴ was cleaner. Since the submission of the initial version of our paper, Professor W. S. Johnson has kindly communicated results from his laboratory involving the formation of steroids using propargylsilane terminators. The

Table I. Rates of Acetolysis of Silylated and Unsilylated Tosylates and Relative Percent Cyclization

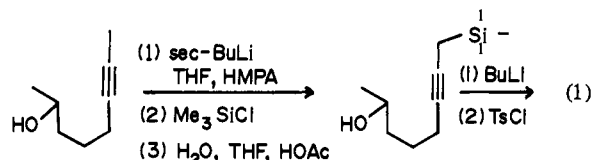
tosylate	cyclization, $k \times 10^5$,		k_{Si}/k_H
	%	s ⁻¹	
6-heptyn-2-yl	26	3.18 ^a	1.42
7-(trimethylsilyl)-6-heptyn-2-yl, 5	38	4.4	
6-octyn-2-yl	60	9.71 ^b	1.20
		12.2 ^c	
		12.7 ^d	
8-(trimethylsilyl)-6-octyn-2-yl, 1	77	15.3	

^a Data from ref 1b. ^b Data from ref 1b. Examination of the original notebook shows that the plot did not take into account the reported 11% of rearranged tosylate. ^c Original data recalculated to take into account the rearranged tosylate. ^d Redetermined value (this study).

advantageous stereochemical aspects are borne out by Johnson's results.

Several studies which have some relationship to ours are to be noted. In a polyolefinic cyclization involving an aromatic terminator, a concerted cyclization was implied by the observed effect of aromatic substituents.¹¹ It appeared that charge was relayed to the remote aromatic ring although the Hammett plot was curved, necessitating the postulation of an unidentified equilibrium process prior to the final cyclization step. In a study of "relay-participation", in which the delocalization of transition-state charge to remote sites could occur through simultaneous reaction of two double bonds,^{12a} the meaning of the results is still the subject of debate.^{12b} Our study may be said to show that hyperconjugative relay participation by silicon-carbon bonds is not a large effect in the instances which we investigated. Johnson, in his recent review,^{4b} cites unpublished instances in which changing the nucleophilicity of the terminator led to small rate effects.

Since the literature contains little information regarding the synthesis of propargylsilanes,¹³ it is of interest to mention our methods. Dilithiation of 6-octyn-2-ol with *sec*-butyllithium followed by bis(trimethylsilylation) and hydrolysis of Me₃SiO gave 8-(trimethylsilyl)-6-octyn-1-ol (eq 1). This alcohol was cleanly



separated (as shown by ¹³C NMR) from 6-octyn-2-ol and a terminally silylated alkyne by reverse-phase chromatography on an analytical column. The terminally silylated analogue **5** was prepared by a similar sequence from 6-heptyn-2-ol.

Of more significance to future studies is the clean preparation of (propargyltrimethyl)silanes which we have achieved by using (trimethylsilyl)methyl triflate, whose convenient preparation from Me₃SiCH₂Cl we have reported.¹⁴ The experimental procedure for obtaining 1-(trimethylsilyl)-2-nonyne, (CH₃)₃SiCH₂C≡C-(CH₂)₅CH₃, follows.

To 1-octyne (2.33 g, 21.2 mmol) in 50 mL of ether at -78 °C was added 21.2 mmol of butyllithium (Aldrich, 1.5 M in hexane) and 3.80 g of hexamethylphosphoramide (*carcinogen!*). (Tri-

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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 H₂O (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); ¹H NMR δ 0.09 [(C-H₃)₃Si], 2.02 (RCH₂C≡C); ¹³C NMR δ -2.06 [(CH₃)₃Si], 7.03 (CH₂Si), 77.25 and 78.92 (C≡C). The ¹³C NMR spectrum showed only one component to be present (>97%). Anal. Calcd for C₁₂H₂₄Si: C, 73.38; H, 12.32. Found: C, 72.96; H, 12.15.

Acknowledgment. Support by the National Science Foundation is gratefully acknowledged (Grants CH-78-10043 to P.E.P. and CHE 78-18723 for the 400-MHz facility in NMR Spectroscopy at the University of South Carolina).

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Timothy Flood, Paul E. Peterson*

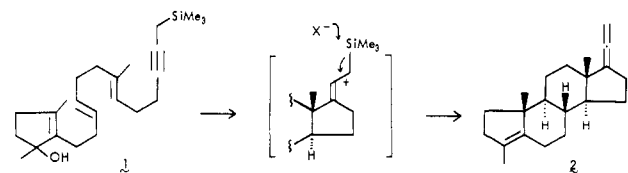
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Received February 28, 1980

Propargylsilane Function as a Terminator of Biomimetic Polyene Cyclizations Leading to Steroids^{1,2}

Sir:

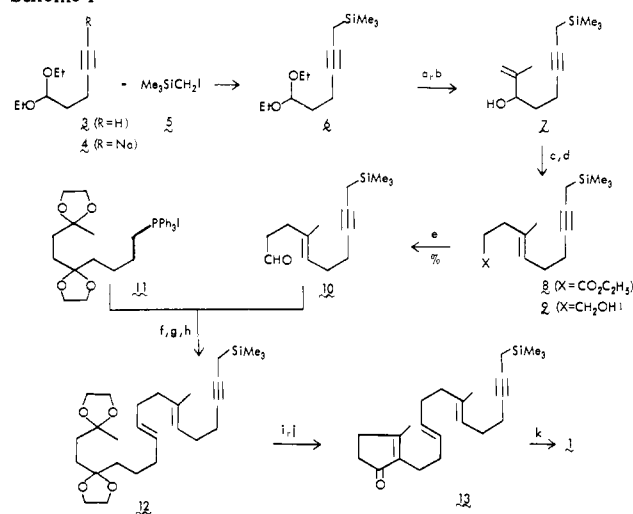
The recent discovery that the allylsilane residue can serve as an efficient function for terminating biomimetic polyene cyclizations³ has prompted us to examine the related system in which the allylsilane is replaced by the propargylsilane moiety. This latter function, when positioned as in formula 1, 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 1), the key step being the Wittig-Schlosser condensation of the known phosphonium salt 11⁶ with the aldehyde 10. Scheme

Scheme 1



^a To give the aldehyde: 5:1 THF/10% HCl, 27 °C, 2 h. ^b 2.8 mol equiv of CH₂=C(CH₃)MgBr, THF, -5 °C, 1.5 h. ^c To give 8: 11.6 mol equiv of CH₃C(OEt)₃, 0.2% C₆H₅CO₂H, 130 °C, 40 min. ^d To give 9: 1.5 mol equiv of LiAlH₄, THF, 0 °C, 3 h. ^e 2.3 mol equiv of (C₆H₅NH)₂Cr₂O₇, CH₂Cl₂, 22 °C, 24 h. ^f 11 + 0.82 mol equiv of C₆H₅Li, THF, 0 °C, 15 min. ^g 0.68 mol equiv of 10, -78 °C, 1 h. ^h 0.89 mol equiv of C₆H₅Li, Et₂O, -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, Et₂O, 0 °C (four treatments).

1 is analogous to the one already described in detail for the preparation of the de(trimethylsilyl) substrate (1 with H in place of Me₃Si).⁶

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)trimethylsilane⁸ 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 reaction¹¹ 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 dichromate¹² 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). Deke-talization 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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