electron-transfer reactions of $O_2^-\cdot$ mimic nucleophilic attack, as has been shown to occur in the reaction of $O_2^-\cdot$ with nitro substituted aromatic halides.[10a,34] In these instances, $O_2^-\cdot$ reduces the compound to form a one-electron reduced intermediate, which then reacts with molecular oxygen. This type of mechanism would require the production of DMPO–e⁻ as a free intermediate. However, DMPO–e⁻ is known to rapidly protonate to form the hydrogen atom adduct, DMPO–H.[2] DMPO–H formation was not observed in the current study, thus ruling out this reaction mechanism as a possibility.

The spin-trapping (i.e., radical addition) reaction is not the only way in which $O_2^-\cdot$ can react with nitrones; an ionic mechanism is also possible. Therefore a possible explanation for the lower rate of $O_2^-\cdot$ addition to DMPO, as compared to $HO_2\cdot$, is that $O_2^-\cdot$ reacts primarily by an ionic mechanism. To the best of our knowledge, this is the first study to report kinetic data on the addition of superoxide to a double bond, and there is little information in the literature with which to compare our observations.

The extent to which an ionic mechanism participates in adduct formation is dependent upon the nucleophilicity of $O_2^-\cdot$ in aqueous solution and the susceptibility of DMPO to nucleophilic attack. Danen and Warner have reported rates of nucleophilic displacement of $O_2^-\cdot$ with alkyl bromides in DMSO; the rates they reported ranged from $<1\ M^{-1}\ s^{-1}$ to $6.7 \times 10^2\ M^{-1}\ s^{-1}$ at 25 °C.[7] Although one group has reported that $O_2^-\cdot$ can act as a nucleophile in an aqueous system,[9] Fee and Valentine have argued that the nucleophilicity of $O_2^-\cdot$ would be expected to be greatly decreased in water by analogy to the effect of solvation on the nucleophilicity of fluoride ion.[8] DMPO is known to undergo nucleophilic additions in both aqueous[35] and nonaqueous systems.[12] Thus further study is required in order to determine if $O_2^-\cdot$ reacts with DMPO by means of an ionic or radical mechanism, or a combination of both reaction pathways.

Acknowledgments. This work was supported in part by grants from the National Institutes of Health, GM 25753 and GM 25188.

---

(34) Frimer, A.; Rosenthal, I. *Tetrahedron Lett.* **1976**, 2809–2812.

(35) Evans, C. A. *Aldrichimica Acta* **1979**, *12*, 23–29.

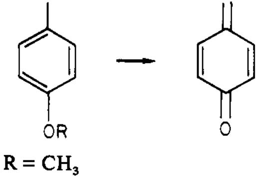
Oxidation of Hydroquinone Silyl Ethers to Quinones

Ray F. Stewart[1] and Larry L. Miller*

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received January 31, 1980*

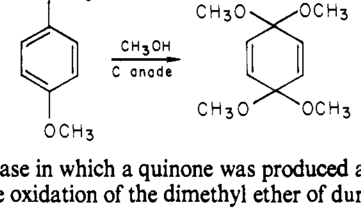
Abstract: The electrochemical oxidation of trialkylsiloxybenzene derivatives was investigated using platinum and graphite anodes in either acetonitrile or methylene chloride solvent. Preparative oxidation of the bis(trimethylsilyl) ethers of hydroquinone, chlorohydroquinone, 2,5-di-*tert*-butylhydroquinone, and 9,10-dihydroxyanthracene gave the corresponding quinones in 80–90% yield. Oxidation of 1,4-bis(trimethylsiloxy)-2-methoxybenzene in acetonitrile gave 3,6-dihydroxy-2,7-dimethoxydibenzofuran in 65% yield. Oxidation of 1-methoxy-4-(trimethylsiloxy)benzene in methanolic acetonitrile produced 1,1-dimethoxy-2,5-cyclohexadien-4-one in 99% yield. The cyclic voltammograms of the trimethylsilyl, triethylsilyl, and *tert*-butyldimethylsilyl ethers of 2,5-di-*tert*-butylhydroquinone were recorded using acetonitrile and methylene chloride solvents at 25 and –60 °C. These compounds were found to react by initial one-electron oxidation to generate a cation radical which decomposes by silicon–oxygen bond cleavage to eventually form quinone. The relative rates for decomposition of the trimethylsilyl, triethylsilyl, and *tert*-butyldimethylsilyl ether cation radicals at –60 °C were 10:5:1. *tert*-Butyldimethylsilyl chloride and *tert*-butyldimethylsilyl triflate were found to be stable toward cathodic reduction in dry methylene chloride and acetonitrile at potentials as negative as –2.1 vs. Ag/0.1 M $AgNO_3$. Cyclic voltammetry indicated that reduction of 2,5-di-*tert*-butylbenzoquinone, anthraquinone, and naphthoquinone in the presence of *tert*-butyldimethylsilyl chloride resulted in reductive silylation.

The quinone/hydroquinone couple is the classic organic redox system and, because this interconversion is so facile, quinones and hydroquinones are widely used both naturally and in man-made products.[2] We felt that a reaction which cleanly converted a nonphenolic compound into a quinone would find utility in a variety of applications. We have, therefore, considered masking hydroquinones as diethers and releasing them by oxidation, e.g., eq 1. The importance of this reaction has already been recognized and the oxidative conversion of 1,4-dimethoxy aromatics to quinones has been accomplished in yields of 50–90% using AgO in acidic dioxane.[3] The present study employed anodic oxidation and there is a report that oxidation of **1a** on a PbO_2 anode in sulfuric acid produced quinone in 49% yield.[4] When nonaqueous electrochemical solvents are used, quinone formation is not observed and instead dimerization or nucleophilic attack at a ring position dominates.[5] A reaction of this type[6,7] which has provoked some synthetic interest is eq 2.



(1)

1a, R = CH_3
b, R = $(CH_3)_3Si$



(2)

A special case in which a quinone was produced anodically from an ether is the oxidation of the dimethyl ether of durohydroquinone

---

(1) Taken in part from the Ph.D. Thesis of Ray F. Stewart, University of Minnesota.

(2) Patai, S., Ed. "The Chemistry of the Quinoid Compounds"; Wiley: New York, 1974.

(3) Snyder, C. D.; Rapoport, H. *J. Am. Chem. Soc.* **1972**, *94*, 227.

(4) Fichter, F.; Dietrich, W. *Helv. Chim. Acta* **1924**, *7*, 131.

(5) Weinberg, N. L., Ed. "Techniques of Electroorganic Synthesis"; Wiley: New York, 1974; Part I.

(6) Belleau, B.; Weinberg, N. L. *J. Am. Chem. Soc.* **1963**, *85*, 2525.

(7) Manning, M. S.; Raynolds, P. W.; Swenton, J. S. *J. Am. Chem. Soc.* **1976**, *98*, 5008. Manning, M. J.; Henton, D. R.; Swenton, J. S. *Tetrahedron Lett.* **1977**, 1679.

0002-7863/80/1502-4999$01.00/0

Table I. Voltammetric Data and Oxidation Products from Trialkylsiloxybenzenes[a]

silyl ether	E_p, V[b]	product	% yield[c]
1,4-bis(trimethylsiloxy)benzene (**1b**)	1.10	benzoquinone	86[d]
1,4-bis(trimethylsiloxy)-2-chlorobenzene	1.25	chlorobenzoquinone	80[e]
1,4-bis(trimethylsiloxy)-2,5-di-*tert*-butylbenzene (**3a**)	1.05	2,5-di-*tert*-butylbenzoquinone	92[d]
1,4-bis(*tert*-butyldimethylsiloxy)-2,5-di-*tert*-butylbenzene (**3c**)	1.07	2,5-di-*tert*-butylbenzoquinone	90[e]
1,4-bis(trimethylsiloxy)-2-methoxybenzene	1.05	3,6-dihydroxy-2,7-dimethoxydibenzofuran	65[d]
9,10-bis(trimethylsiloxy)anthracene	0.78	9,10-anthraquinone	92[d]
4-methoxy-1-(trimethylsiloxy)benzene	1.14	1,1-dimethoxy-2,5-cyclohexadien-4-one	99[f]

[a] Platinum working electrode, acetonitrile, 0.1 M lithium perchlorate, 1 mM substrate, scan rate 100 mV s^{-1}, SCE reference electrode. [b] Scan rate $\nu = 100$ mV s^{-1}, SCE reference electrode. [c] Yield of isolated product based on added starting silyl ether. [d] Oxidized in acetonitrile–lithium perchlorate. [e] Oxidized in methylene chloride–tetrabutylammonium tetrafluoroborate. [f] Oxidized in acetonitrile–methanol–lithium perchlorate.

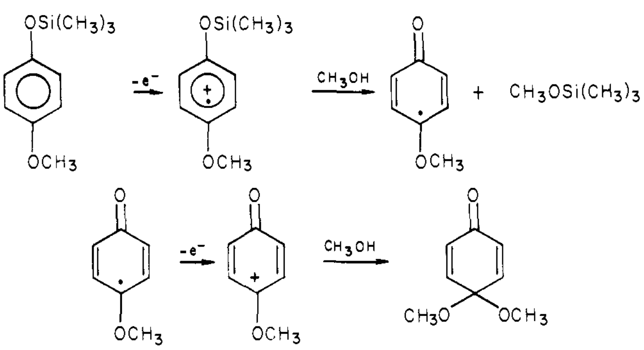
in acetonitrile.[8] In this case, ring substitution is unfavorable and cleavage can compete. The present study probed the utility of silyl ethers in such reactions. Cleavage proved to be extremely facile and quinones were formed in high yield, even at −40 °C.

Results and Discussion

Preparative Oxidation of Hydroquinone Silyl Ethers. Bis(trimethylsilyl) ethers were prepared by treatment of hydroquinones with trimethylsilyl chloride and hexamethyldisilazane in acetonitrile. The sterically hindered *tert*-butyldimethylsilyl and triethylsilyl ethers were prepared by treatment of hydroquinones with the corresponding silyl chlorides and imidazole in dimethylformamide. 1,4-Bis(*tert*-butyldimethylsiloxy)-2,5-di-*tert*-butylbenzene was especially difficult to prepare and in this case *tert*-butyldimethylsilyl triflate was used. As described in the Experimental Section, this reagent is readily synthesized and as expected it is a very reactive silylating agent. It would appear to be an attractive alternative to the perchlorate ester.[9] Crystalline silyl ethers were purified by recrystallization from acetonitrile. Liquid compounds were purified by vacuum distillation or column chromatography. All of the silyl ethers used in this study were stable toward hydrolysis when purified and could be stored for several months without noticeable decomposition.

Oxidations were carried out at a platinum foil or carbon felt anode in a three-compartment cell equipped with an SCE reference electrode and a stainless-steel cathode. The anode potential was usually set 100 mV anodic of the peak potential (E_p) as measured by cyclic voltammetry, and electrolysis was terminated after the current decayed smoothly to background with passage of 2.0–2.2 F mol^{-1}. Similar coulometric results were obtained using either acetonitrile containing lithium perchlorate or methylene chloride containing tetrabutylammonium perchlorate or tetrafluoroborate. Products were isolated, recrystallized, and identified by their melting points and spectra. As shown in Table I, good yields of quinones were generally obtained. In the case of **1b**, quinone yields of >85% were obtained using either carbon or platinum anodes in either acetonitrile or methylene chloride solvent.

Scheme I



The data suggest that silylation–oxidation will be a high-yield procedure for masking and revealing quinone functions in complex molecules. This approach may find utility in synthesis because (a) hindered silyl ethers are stable to the many reaction conditions, (b) the oxidation conditions are very mild, and (c) the deprotection step should be very selective. Of the common functional groups only amines and thiols would be expected to be oxidized at this potential.

The reductive silylation of quinones was also studied. Cyclic voltammetry showed that the reduction of **3a**, anthraquinone, or naphthoquinone in methylene chloride containing *tert*-butyldimethylsilyl chloride gave reductive silylation. Specifically, in the absence of this silyl chloride a reversible quinone couple was observed. In its presence there was no reversibility and instead an anodic peak corresponding to the disiloxy compound was observed. Although this was encouraging, these reactions have not been performed on a preparative scale. We have previously shown that trimethylsilyl chloride reacts directly with unhindered benzoquinones to produce chlorodisiloxybenzenes[10] and this aborted the possibility of simple reductive silylation for most quinones.

In contrast to these results for 1,4-disiloxybenzene oxidations, it was found that 1,4-dimethoxybenzene and 2,5-di-*tert*-butyl-1,4-dimethoxybenzene did not produce quinones under these oxidation conditions. Thus, it is proposed that quinone formation results from the facile cleavage of the silicon–oxygen bond in the disiloxy aromatic cation radical. As a test of this proposal, the oxidation of 1-methoxy-4-(trimethylsiloxy)benzene was performed in methanol containing lithium carbonate. Since 1,4-dimethoxybenzene gives the bisketal of benzoquinone under these conditions,[5-7] it seemed that we could obtain a bisketal, quinone or 4,4-dimethoxycyclohexadienone. The latter was observed and, although a mixed bisketal, 1,1,4-trimethoxy-4-(trimethylsiloxy)benzene, could have formed and been hydrolyzed, we feel that this is unlikely since the oxidation was carried out in the presence of lithium carbonate. In addition, direct GLC analysis of the anolyte showed only the monoketal and unreacted starting material. The monomethyl ether of hydroquinone was not detected in the anolyte, indicating that the silyl ether was indeed the substance being oxidized. Therefore, we propose the mechanism in Scheme I involving nucleophilic attack at silicon rather than carbon.

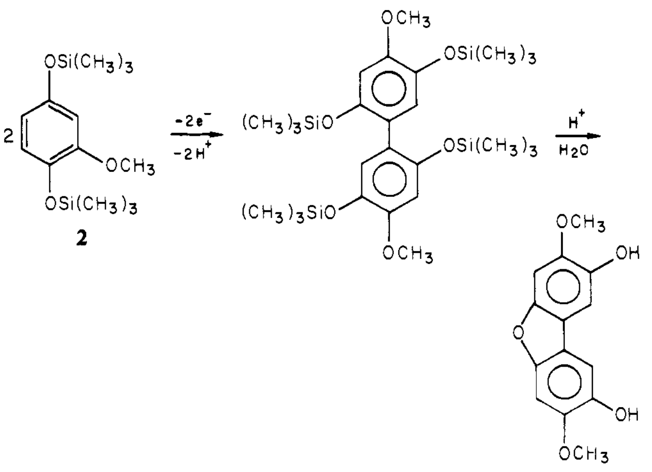
In only one case was a simple siloxy to carbonyl transformation not observed. Oxidation of 2-methoxy-1,4-bis(trimethylsiloxy)benzene (**2**) in acetonitrile–lithium perchlorate produced a bright red material which could be seen streaming off the electrode. In contrast to the other oxidations, this electrolysis consumed only 1 F mol^{-1}. Workup in the usual manner gave tan plates of a sparingly soluble compound which could be recrystallized from chloroform. NMR analysis indicated a methoxyl group, two aromatic hydrogens, and an exchangeable phenolic proton. Mass-spectral and combustion-analysis data indicated the formula $C_{14}H_{12}O_5$, from which structure **4** was deduced. Presumably this result is due to the introduction of a methoxy substituent which is known to favor dimerization at the para position. Oxidation of 2,4,5-trimethoxybenzene, for example, gives 2,2′,4,4′,5,5′-

---

[8] Parker, V. D. *Chem. Commun.* **1969**, 610.

[9] (a) Trimethylsilyl perchlorate is a covalent compound and has recently been used as a very reactive blocking agent for the protection of hindered alcohols. Marsmann, H. C.; Horn, H. G. *Z. Naturforsch., B* **1972**, *27*, 1448. (b) Barton, T. J.; Tully, C. R. *J. Org. Chem.* **1978**, *43*, 3649.

[10] Miller, L. L.; Stewart, R. F. *J. Org. Chem.* **1978**, *43*, 3078.



2

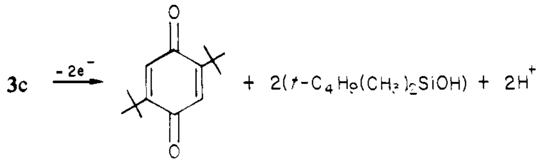
4

hexamethoxybiphenyl.[11] In addition, introduction of a methoxy group should stabilize the cation radical of **2** allowing dimerization to compete successfully with trialkylsilyl cleavage.

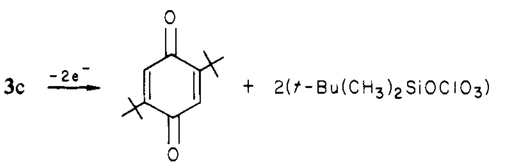
Cyclic Voltammetry. Using either acetonitrile or methylene chloride solvent, the cyclic voltammetric results for all the disiloxybenzenes were very similar to those described here for compounds **3a–c**. These silyl ethers were chosen for quantitative studies because the corresponding dimethyl ether had been found to produce a very stable cation radical and this provided a convenient way to compare the reactivities of the cation radicals from alkyl and silyl ethers. Electrochemical measurements were carried out in 0.2 M tetrabutylammonium perchlorate–methylene chloride solvent using a platinum working electrode and a Ag/0.1 M $AgNO_3$ reference electrode.

The trimethylsilyl, triethylsilyl, and *tert*-butyldimethylsilyl ethers of 2,5-di-*tert*-butylhydroquinone, **3a–c**, gave essentially identical voltammograms. As an example, the voltammogram of trimethylsilyl ether **3a** in nominally dry methylene chloride at room temperature and $\nu = 0.5$ V s^{-1} gave an anodic peak, $E_{pa} = 0.87$ V. No cathodic peak due to cation radical reduction was seen even at 10 V s^{-1}. A plot of the anodic peak current, I_{pa}, against concentration gave a straight line through the origin as did a plot of I_{pa} vs. $\nu^{1/2}$ in the range from 10 to 500 mV s^{-1} (Figure 1). This indicates that the anodic process is first order in **3a** and diffusion controlled.[12]

After traversing the anodic peak at 0.87 V, the voltammograms of all the disilyl ethers showed two couples from anodically generated products: $E_{pc} = -0.38$, $E_{pa} = 0.18$, and $E_{pc} = -1.32$, $E_{pa} = -1.24$ V. The origin of the peak at −0.38 V is proposed to be reduction of anodically generated protic acid. This conclusion is supported by the observation of the same couple when trifluoromethanesulfonic acid was added to a fresh solution of nominally dry methylene chloride–tetrabutylammonium perchlorate. The couple at −1.3 V is due to anodically generated di-*tert*-butylquinone as confirmed from the cyclic voltammogram of this compound.



Drier methylene chloride solutions can be obtained by adding activated alumina.[13] The voltammograms for **3a–c** are changed under these conditions. An example for compound **3c** is shown as Figure 2a. After traversing the anodic peak only a cathodic peak at −1.3 V was seen. When methanol (1%) was added to the solution containing **3c**, the −1.3-V peak became reversible and the proton reduction wave at −0.38 V returned (Figure 2b). This is all in agreement with the above explanations, but it remains to be explained why the −1.3-V peak in the cyclic voltammogram of **3c** is irreversible when aprotic solvent is used, since the quinone is expected to be reduced to its anion radical giving a reversible couple. This apparent dichotomy can be resolved by proposing that active silylating reagents, trimethylsilyl perchlorate, for example, are formed in the anodic process and they scavenge the quinone anion radicals. In agreement with this proposal, the cyclic voltammogram for the reduction of di-*tert*-butylquinone in the presence of *tert*-butyldimethylsilyl chloride is irreversible and has an oxidation wave on the positive-going half-cycle which corresponds to oxidation of **3c**.



No attempt was made to isolate trialkylsilyl perchlorates from anolytes because of their extreme reactivity and thermal instability. Trialkylsilyl alcohols and their product disilyl ethers were, however, detected as products from electrolysis. It was a concern in this regard to know if silyl perchlorates or silyl triflates should reduce in the potential region examined. No reduction wave was observed

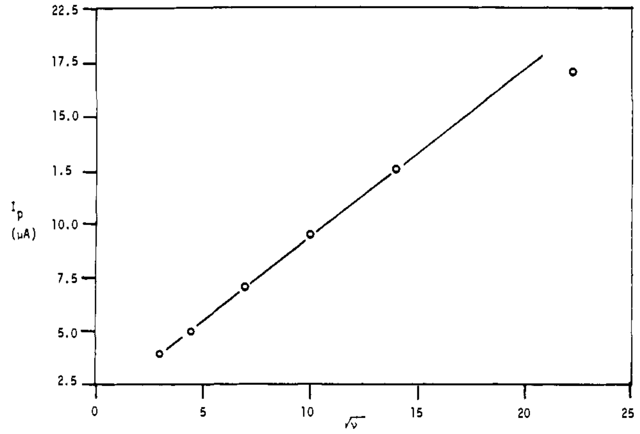


Figure 1. Peak current (I_p) as a function of scan rate for 4.8 mM **3a** in H_2CCl_2, 0.2 M Bu_4NClO_4.

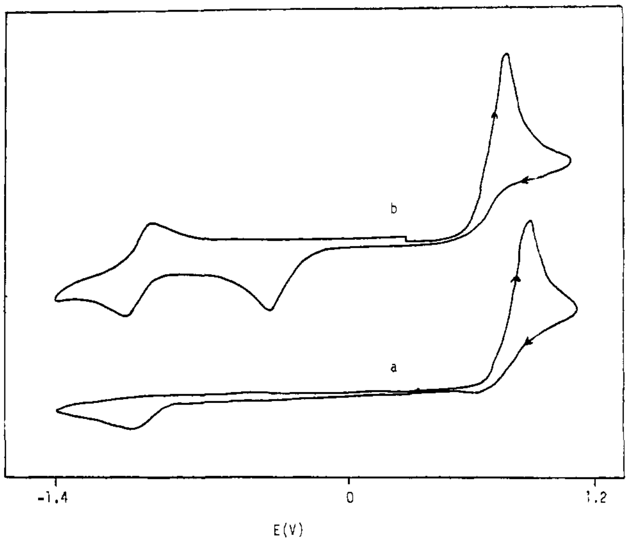


Figure 2. CV of 4.8 mM **3c** in H_2CCl_2, 0.2 M Bu_4NClO_4, Al_2O_3, $\nu = 0.5$ V s^{-1}. Curve a, dry solution; curve b, added 1% methanol.

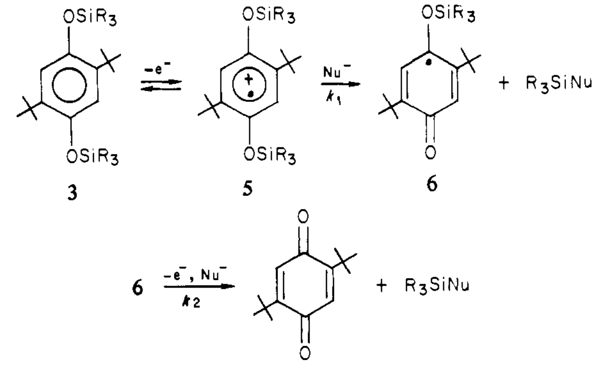
---

[11] Erdtmann, H. G. H. *Proc. R. Soc. London, Ser. A* **1934**, *143*, 191.

[12] Macdonald, D. "Transient Techniques in Electrochemistry"; Plenum Press: New York, 1977.

[13] Addition of alumina (Woelm W-200) to the cyclic voltammetry cell, followed by stirring, has been shown to provide relatively dry conditions. Parker, V. D.; Hammerich, O. *Electrochim. Acta* **1973**, *18*, 537.

Scheme II



3a, $R_3 = (CH_3)_3$
b, $R_3 = (CH_3CH_2)_3$
c, $R_3 = t\text{-}C_4H_9, (CH_3)_2$

for either *tert*-butyldimethylsilyl chloride or *tert*-butyldimethylsilyl trifluoromethanesulfonate in the region of 0.5 to −2.1 V in alumina-dried solutions while nominally dry solutions showed a reduction wave around −0.38 V.

The cyclic voltammograms for **3a–c** obtained using acetonitrile solvent were analogous to those in methylene chloride. Thus, nominally dry solvents gave a proton reduction peak at −0.50 V vs. Ag/0.1 M $AgNO_3$ and the quinone reduction peak at −0.97 V. Drier solutions did not show the proton reduction wave. The interpretation that the −0.5-V couple in CH_3CN solvent is due to protons disagrees with a published interpretation offered by Boberski and Allred,[14] but agrees with the recent report of Corriu, Dabosi, and Martineau.[15]

The most intriguing aspect of these results is that no evidence for the cation radical derived from **3** (or from **1b**) could be obtained in either solvent even at 10 V s^{-1}. This indicates that it is very much more reactive than the cation radical from 2,5-di-*tert*-butyl-1,4-dimethoxybenzene, which does not react after many seconds under these conditions. It strongly suggests that the siloxy cation radical (**5**) reacts by cleavage of the silicon–oxygen bond. This probably involves attack on silicon by a nucleophile[16] (Scheme II).

Low-Temperature Cyclic Voltammetry. Since cation **5** could not be detected at room temperature, low temperatures were employed to slow down its chemical reaction. This allowed a more quantitative comparison of the reaction rates for methyl and silyl ethers and allowed a direct measurement of the rate of cleavage for different trialkylsilyl groups.

Using dried methylene chloride solvent and lowering the temperature to −60 °C caused the oxidation of **1b** and **3a–c** to become quasi-reversible at scan rates greater than 100 mV s^{-1}. A typical voltammogram for **3a–c** or for ferrocene at −60 °C and $\nu = 200$ mV s^{-1} showed $E_{pa} - E_{pc} = 90$ mV and the ratio of anodic and cathodic peak currents $I_{pa}/I_{pc} = 1.0$. Cyclic voltammograms were then recorded at varying ν from 10 to 1000 mV s^{-1}. Plotting I_{pc}/I_{pa} vs. log ν gave curves which closely matched the theoretical curve[11,17] for a process involving reversible electron transfer followed by an irreversible step (Figure 3). This interpretation was also supported by an analysis of the ν dependence of I_{pa}.[12,18] Qualitatively, $I_{pa}\nu^{-1/2}$ increased with decreasing ν, indicating a one-electron process at high ν. All this data is consistent with Scheme II. Since the voltammograms approach reversibility at fast sweep rates, it is possible to determine the rate constant for silyl transfer, k_1, according to the procedure given by Nicholson and Shain.[18] The assumption has been made that $k_2 > k_1$ since the radical **6** is expected to oxidize more easily than disilyl ether **3**. Also, we have assumed that the decomposition reaction is first order in cation radical and that, although the overall reaction is a two-electron process, it can be treated as a simple EC process as it approaches reversibility. Nicholson and Shain have reported that nearly identical working curves are obtained for both EC and ECEC processes.[18]

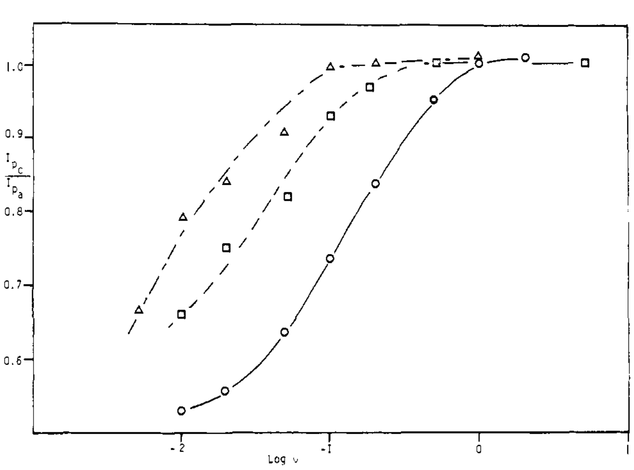
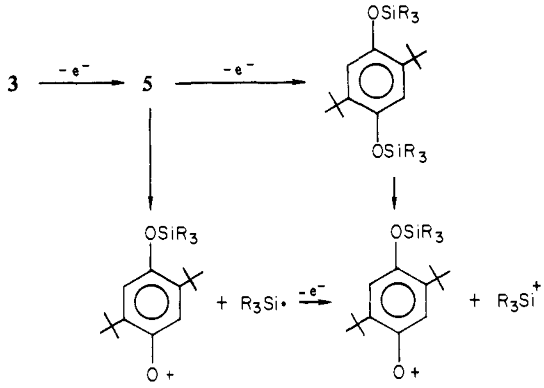


Figure 3. Ratio of cathodic to anodic peak currents as a function of sweep rate (ν) for compounds **3a**, ○; **3b**, □; **3c**, △.

Scheme III



Measurement of precise rate constants at this temperature was complicated by the low conductivity of the medium. Because the increased *iR* drop causes distortion of the wave shape, particularly at fast scan rates, we chose to measure relative rate constants k_1' for the three silyl ethers from the I_{pc}/I_{pa} vs. ν plot. In this manner the decrease in peak currents due to *iR* drop in the anodic and cathodic half-cycles would tend to cancel each other as the couple approaches reversibility and the relative rates should be quite reliable. As shown in Figure 3, the relative rates of cleavage are trimethylsilyl > triethylsilyl > *tert*-butyldimethylsilyl with the relative magnitudes being 10, 5, and 1, respectively. It was also observed that addition of 1% methanol greatly enhanced the rate of reaction of the cation radical (**5**). All these data are consistent with the general proposal (Scheme II) that the cation radical reaction involves nucleophilic attack on silicon and silicon–oxygen bond cleavage. This reaction is extremely rapid even when the only apparent nucleophile is perchlorate. It is noted that *tert*-butyltrimethylsilyl triflate is covalent and stable in methylene chloride–tetrabutylammonium perchlorate at room temperature and the cation radical **5** reacts in less than 1 s at −60 °C. These data suggest that the phenoxy radical is a far better leaving group than triflate. Since the latter has been widely recognized and utilized as a "super" leaving group it would also seem that phenoxy radical should be so classified.

The precise mechanism of silicon–oxygen cleavage is of interest but may be quite complex. Several possibilities are shown in Schemes III and IV. Realizing that these or alternative schemes must be completed to include the second cleavage step and that

---

[14] Boberski, W. G.; Allred, A. L. *J. Organomet. Chem.* **1975**, *88*, 65.

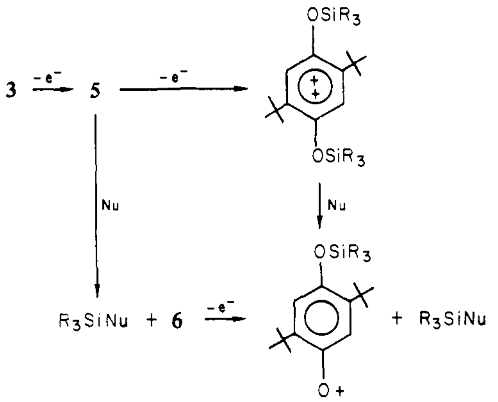
[15] Corriu, R. J. P.; Dabosi, G.; Martineau, M. *J. Chem. Soc., Chem. Commun.* **1978**, 457.

[16] Sommer, L. H. "Stereochemistry, Mechanism and Silicon"; McGraw-Hill: New York, 1965.

[17] Byrd, L.; Miller, L. L.; Pletcher, D. *Tetrahedron Lett.* **1972**, 2419.

[18] (a) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706. (b) *Ibid.* **1965**, *37*, 178, 190.

Scheme IV



one must be concerned with solution-phase disproportionation reactions as well, the mechanism is at present insoluble in detail.

Experimental Section

General. Melting-point determinations are uncorrected, open capillary measurements using a Mel-Temp melting point apparatus. Nuclear magnetic resonance spectra were recorded on a Varian T-60 or CFT 20 instrument. Chemical shifts were measured relative to tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer 727 B or 297 spectrophotometer. Mass spectra of analytical samples were recorded on an AEI MS-30, while gas chromatography–mass spectra (GLC–MS) analyses were obtained on a Hitachi RMU-60X instrument. Combustion analyses were obtained from M-H-W Laboratories, Phoenix, Ariz.

Analytical thin layer chromatography (TLC) was performed using 0.25-mm-thick precoated TLC plates with fluorescent indicator, distributed by Brinkmann Instruments, Inc. Gas–liquid chromatographic analysis (GLC) of product mixtures was carried out on a Varian Model 3700 gas chromatograph utilizing a flame ionization detector. Peak areas were determined with a Perkin-Elmer M-2 calculating integrator.

Cyclic Voltammetry. Cyclic voltammetry was carried out using a Princeton Applied Research (PAR) Model 173 potentiostat in conjunction with a PAR Model 175 universal programmer. Voltammograms were recorded on a Houston 1000 X-Y recorder for sweep rates (ν) less than 0.5 V s^{-1}. Faster sweep rates were recorded on a Tektronix 5110 dual channel storage oscilloscope. The cyclic voltammetry cell was a 25-mL 14/20 three-neck round-bottom flask equipped with a gas inlet tube and Luggin capillary. The working electrode was a platinum wire (18 gauge) which was sealed in Pyrex and polished to a smooth disk. The counterelectrode was a sheet of platinum foil and the reference electrode was either a Radiometer saturated calomel electrode (SCE) or a silver wire immersed in a 0.1 M silver nitrate solution (Ag/0.1 M $AgNO_3$) separated from the bulk solution by a fine glass frit.

Preparative Electrochemical Oxidations. Preparative oxidations were carried out with a PAR Model 373 potentiostat in conjunction with a Model 212-XL-1 integrator–totalizer manufactured by Acromag Inc., Wixom, Mich. The electrolysis vessels were two-compartment H-type cells with a medium-porosity glass frit as cell divider. Anolyte capacities ranged from 300 to 75 mL while catholyte capacities ranged from 100 to 25 mL. Electrolysis vessels were fitted with tops which had standard 14/20 joints to allow positioning of electrodes and to accommodate drying and gas inlet tubes.

Spectro-Tech graphite electrodes ($^1/_4$ × 4 in., no. 731252) were obtained from Ultra Carbon Corp., Bay City, Mich., and graphite felt ($^1/_4$ in., grade GF) was purchased from Carborundum Co., Niagara Falls, N.Y. Reference electrodes were either a commercial SCE or a Ag/0.1 M $AgNO_3$ electrode prepared as previously described.

Acetonitrile used as electrolysis solvent was Baker Analyzed LC grade, contained 0.001% water, and was generally suitable for use without further treatment. Acetonitrile was dried further by passage through a 1.5 × 12 in. column of activated alumina. GLC analysis indicated that this reduced the moisture content to about 5 mM. Methylene chloride used as electrolysis solvent was fractionally distilled from calcium chloride and stored over PA 400 silica gel obtained from Davison Chemical Co. Supporting electrolytes were obtained from Southwestern Analytical Chemicals, Inc., Austin, Texas, or from Tridom Fluka Chemical, Inc., Hauppauge, N.Y., and were routinely kept in a desiccator but were not dried further.

1,4-Bis(trimethylsiloxy)benzene (1b). To a stirred solution of 1.65 g (0.015 mol) of hydroquinone in 25 mL of dry acetonitrile were added via syringe 1.19 g (0.01 mol) of chlorotrimethylsilane and 1.77 g (0.01 mol) of hexamethyldisilazane. The reaction mixture was stirred under argon for 12 h, filtered, reduced in vacuo, dissolved in 100 mL of pentane, washed with saturated bicarbonate and brine solutions, and dried over $MgSO_4$. Filtration and removal of solvent yielded 3.47 g (91%) of crude product. Recrystallization from heptane yielded long, white needles of 1,4-bis(trimethylsiloxy)benzene: mp 56 °C (lit.[19] 49 °C); IR (Nujol) 1230, 910, 840, 750 cm^{-1}; NMR (acetone-d_6) δ 0.20 (s, 18 H), 6.65 (s, 4 H); mass spectrum *m/e* (rel intensity) 255 (20), 254 (80, M$^+$), 240 (24), 239 (100), 112 (19), 73 (33).

1,4-Bis(trimethylsiloxy)-2-methoxybenzene (2). To a stirred solution of 7.0 g (0.05 mol) of methoxyhydroquinone in 50 mL of dichloromethane under an argon atmosphere were added via syringe 3.63 g (0.03 mol) of chlorotrimethylsilane and 5.4 g (0.033 mol) of hexamethyldisilazane. A white precipitate was formed and the reaction mixture was stirred for 8 h. The reaction mixture was filtered and the precipitate was rinsed with 100 mL of dichloromethane. The combined organic layers were rinsed with 2 × 25 mL of ice-cold water, followed by 2 × 15 mL of bicarbonate solution. Drying over $MgSO_4$ followed by filtration and removal of solvent in vacuo yielded 13.4 g (94.5%) of 1,4-bis(trimethylsiloxy)-2-methoxybenzene: bp 265 °C; IR (neat) 3000–2800, 1580, 1500–1400 (three bands), 1300, 1250, 1190, 1150, 1100, 1020, 960, 910, 740 cm^{-1}; NMR ($CDCl_3$) δ 6.73–6.21 (m, 3 H), 3.76 (s, 3 H), 0.23 (s, 9 H), 0.17 (s, 9 H); mass spectrum *m/e* (rel intensity) 286 (12), 285 (20), 284 (84, M$^+$), 254 (100), 212 (21), 147 (36), 122 (20), 75 (60), 73 (87). Anal. Calcd for $C_{13}H_{24}O_3Si_3$: C, 54.88; H, 8.50. Found: C, 54.72; H, 8.72.

9,10-Bis(trimethylsiloxy)anthracene was prepared as above from 9,10-dihydroxyanthracene, mp 121–122 °C (lit.[19] 120–121 °C).

1,4-Bis(trimethylsiloxy)-2,5-di-*tert*-butylbenzene (3a) was prepared in 78% yield from 2,5-di-*tert*-butylhydroquinone by the same method as 1,4-bis(trimethylsiloxy)benzene, and recrystallized from acetonitrile: mp 132–133 °C; IR (Nujol) 1340, 1220, 1190, 905, 820 cm^{-1}; NMR ($CDCl_3$) δ 0.30 (s, 18 H), 132 (s, 18 H), 6.66 (s, 2 H); mass spectrum *m/e* (rel intensity) 368 (9), 367 (24), 366 (74, M$^+$), 352 (18), 351 (57), 73 (100), 57 (25); calcd for $C_{20}H_{38}O_2Si_2$ 366.2410, measd 366.2394. Anal. Calcd for $C_{20}H_{38}O_2Si_2$: C, 65.51; H, 10.45. Found: C, 65.66; H, 10.53.

1-(Trimethylsiloxy)-4-methoxybenzene was prepared in good yield by silylation of hydroquinone monomethyl ether with trimethylsilyl chloride and hexamethyldisilazane in acetonitrile as above.[20] Distillation at the water pump yielded pure product: IR (neat) 2910, 2800, 1485, 1440, 1420, 1220, 1020, 900, 830, 720 cm^{-1}; NMR ($CDCl_3$) δ 0.23 (s, 9 H), 3.74 (s, 3 H), 6.76 (s, 4 H); mass spectrum *m/e* (rel intensity) 197 (13), 196 (78, M$^+$), 182 (16), 181 (100), 75 (10), 73 (42). Anal. Calcd for $C_{10}H_{16}O_2Si$: C, 61.18; H, 8.22. Found: C, 61.11; H, 8.26.

1,4-Bis(triethylsiloxy)-2,5-di-*tert*-butylbenzene (3b) was prepared by treatment of 2,5-di-*tert*-butylhydroquinone with triethylsilyl chloride and imidazole in dimethylformamide according to the standard procedure. Workup gave an oil which contained three major compounds via TLC (SiO_2, heptane, R_f 0.7, 0.2, and 0.1). Column chromatography on silica gel (60–200 mesh), eluting with heptane, gave a 35% yield of 1,4-bis(triethylsiloxy)-2,5-di-*tert*-butylbenzene (**3b**) as a clear liquid which crystallized only after standing for several days: mp 54 °C; IR (neat) 2950, 2900, 2860, 1500, 1360, 1230, 1205, 923, 720 cm^{-1}; NMR ($CDCl_3$) δ 8.66 (s, 2 H), 1.34 (s, 18 H), 0.96 (m, 30 H); mass spectrum *m/e* (rel intensity) 452 (14), 451 (38), 450 (83, M$^+$), 436 (14), 435 (31), 105 (100); calcd for $C_{26}H_{50}O_2Si_2$ 450.3349, measd 450.3344. Anal. Calcd for $C_{26}H_5O_2Si_2$: C, 69.27; H, 11.18. Found: C, 69.16; H, 10.99.

***tert*-Butyldimethylsilyl Trifluoromethanesulfonate.** To a solution of 31.5 g (0.21 mol) of *tert*-butyldimethylsilyl chloride in 25 mL of heptane was added 30 g (0.20 mol) of trifluoromethanesulfonic acid. The mixture was refluxed under argon until no more gas was evolved (20 h). Distillation afforded 48.2 g (89%) of *tert*-butyldimethylsilyl trifluoromethanesulfonate as a clear, fuming liquid: bp 180 °C; NMR ($CDCl_3$) δ 0.45 (s, 6 H), 1.00 (s, 9 H); mass spectrum *m/e* (rel intensity) 207 (26, M$^+$ – *tert*-butyl), 77 (100), 75 (62), 73 (31), 57 (40), 50 (31); calcd for $C_3H_6F_3O_3SiS$ 206.9741, measd 206.9750.

1,4-Bis(*tert*-butyldimethylsiloxy)-2,5-di-*tert*-butylbenzene (3c). In a 100-mL reaction flask were placed 2.22 g (1.0 mmol) of 2,5-di-*tert*-butylhydroquinone, 20 mL of chloroform, and 2.4 g (2.2 mmol) of triethylamine. The flask was flushed with dry argon and cooled to 0 °C. Slowly 5.28 g (2.0 mmol) of *tert*-butyldimethylsilyl trifluoromethanesulfonate was added via syringe and the reaction mixture was stirred overnight at 25 °C. The reaction mixture was poured onto 50 mL of ice water, 100 mL of chloroform was added, and the organic layer was separated, washed with 100-mL portions of 1 N HCl, 1 N NaOH, and saturated bicarbonate, and dried over $CaCl_2$. Filtration and removal of the solvent in vacuo yielded 4.0 g (88%) of crude product. Two recrystallizations from hot acetonitrile gave 2.3 g of **3c**: mp 148–149 °C;

---

(19) Neuman, G.; Neuman W. P. *J. Organomet. Chem.* **1972**, *42*, 277.
(20) We thank K. Rosenblum for preparing this compound.

J. Am. Chem. Soc. **1980**, *102*, 5004-5011

IR (Nujol) 2800, 2950, 1480, 1360, 1215, 1210, 910, 830 cm^{-1}; NMR ($CDCl_3$) δ 0.29 (s, 12 H), 1.02 (s, 18 H), 1.34 (s, 18 H), 6.72 (s, 2 H); mass spectrum *m/e* (rel intensity) 452 (7), 451 (20), 450 (49, M^+), 337 (9), 75 (8), 74 (9), 73 (100), 47 (53), 41 (11); calcd for $C_{26}H_{50}O_2Si_2$ 450.3349, measd 450.3313. Anal. Calcd for $C_{26}H_{50}O_2Si_2$: C, 69.27; H, 11.18. Found: C, 69.46; H, 11.31.

Oxidation of 1,4-Bis(trimethylsiloxy)benzene (1b). The disilyl ether **4** was oxidized at a platinum anode (40 cm^2) in a three-compartment H-type cell (anolyte capacity 100 mL) equipped with a magnetic stirrer, an SCE reference electrode, and a stainless-steel cathode. Solvent–supporting electrolyte was acetonitrile–0.05 M Et_4NBF_4. Background current was less than 1 mA at 1.5 V. Addition of 0.30 g (1.2 mmol) of **1b** resulted in a current of 40 mA which decayed to 2 mA after passage of 2.0 F mol^{-1}. The electrolysis was terminated after 2.1 F mol^{-1}. The anolyte was reduced in vacuo to small volume, and 40 g of chopped ice was added followed by 40 mL of ether. The organic layer was separated, the aqueous layer was extracted with 2 × 20 mL of ether, and the combined organic layers were washed with brine and dried over $MgSO_4$. Filtration and removal of solvent in vacuo gave 0.109 g (86%) of benzoquinone, mp 114 °C, identical in all respects with an authentic sample. Compound **1b** was also oxidized in acetonitrile–$LiClO_4$ and methylene chloride–Bu_4NClO_4, in each case producing benzoquinone in nearly quantitative yield.

Oxidation of 1,4-Bis(trimethylsiloxy)-2-chlorobenzene. 1,4-Bis(trimethylsiloxy)-2-chlorobenzene (1.20 g, 4.17 mmol) was oxidized in acetonitrile–0.1 M $LiClO_4$ at an anode potential of 1.3 V vs. SCE using a graphite felt anode (5 × 2.5 × 0.64 cm). Workup of the anolyte in the usual manner after passage of 2.2 F mol^{-1} yielded 0.63 g of crude product. Recrystallization from hexane gave 0.47 g (80%) of chlorobenzoquinone, mp 57 °C, identical in all respects with an authentic sample.

Oxidation of 9,10-Bis(trimethylsiloxy)anthracene. 9,10-Bis(trimethylsiloxy)anthracene was oxidized at a potential of 1.0 V vs. SCE using a graphite felt anode using acetonitrile–0.1 M $LiClO_4$ as solvent supporting electrolyte. Workup after passage of 2.5 F mol^{-1} gave a 92% yield of anthraquinone, mp 283–285 °C, identical in all respects with an authentic sample.

Oxidation of 1,4-Bis(trimethylsiloxy)-2-methoxybenzene (2). 1,4-Bis(trimethylsiloxy)-2-methoxybenzene (1.42 g, 5 mmol) was oxidized at 1.0 V vs. SCE using a platinum anode (40 cm^2) with acetonitrile–0.2 M $LiClO_4$ as solvent–supporting electrolyte. The reaction was terminated after passage of 1.1 F mol^{-1}. The anolyte was reduced in vacuo and partitioned between methylene chloride and water. The organic layer was washed with water and dried over Na_2SO_4. Filtration and removal of solvent in vacuo yielded 0.47 g of tan crystals. Recrystallization from chloroform gave 0.45 g (65%) of 3,6-dihydroxy-2,7-dimethoxydibenzofuran: mp 180–181 °C; IR (Nujol) 3560, 3520, 3400, 2950, 1640, 1500, 1470, 1450, 1380, 1295, 1150, 915, 850, 815 cm^{-1}; NMR (acetone-d_6) δ 3.95 (s, 6 H), 7.15 (s, 2 H), 7.25 (s, 2 H), 7.28 (s, 2 H); mass spectrum *m/e* (rel intensity) 261 (10), 260 (62, M^+), 246 (16), 245 (100), 230 (22), 217 (10), 202 (15), 44 (30), 40 (40). Anal. Calcd for $C_{14}H_{12}O_5$: C, 64.61; H, 4.64. Found: C, 64.58; H, 4.48.

Oxidation of 4-Methoxy-1-(trimethylsiloxy)benzene. 4-Methoxy-1-(trimethylsiloxy)benzene (0.39 g, 2 mmol) was oxidized at 1.2 V vs. SCE using a platinum anode (40 cm^2) in a solvent–electrolyte solution consisting of 40 mL of methanol, 60 mL of acetonitrile, 1 g of lithium carbonate, and 3 g of lithium perchlorate. The background current was 5 mA. This increased to 220 mA upon addition of substrate and decayed to 9 mA after passage of 2.1 F mol^{-1}. The solvent was reduced in vacuo, combined with 50 mL of methylene chloride, washed with 2 × 10 mL of water and 10 mL of brine, and dried over $CaCl_2$. Removal of solvent in vacuo yielded 0.299 g (99%) of 4,4-dimethoxy-2,5-cyclohexadien-1-one: IR (neat) 2825–2300, 1690, 1640, 1150, 1040, 960, 850 cm^{-1}; NMR ($CDCl_3$) δ 3.41 (s, 6 H), 6.30 (d, 2 H), 6.92 (d, 2 H);[21] mass spectrum *m/e* (rel intensity) 154 (41, M^+), 139 (37), 124 (61), 123 (100), 111 (30), 109 (25), 95 (100), 80 (21), 65 (23), 54 (36), 52 (39), 41 (62); calcd for $C_8H_{10}O_3$ 154.0651, measd 154.0604.

Acknowledgments. This work was supported by the National Science Foundation. Discussion with P. Boudjouck is acknowledged.

---

[21] Nilsson, A.; Ronlan, A. *Tetrahedron Lett.* **1975**, 1107.

Silicon in Synthesis. 10. The (Trimethylsilyl)allyl Anion: A β-Acyl Anion Equivalent for the Conversion of Aldehydes and Ketones into γ-Lactones

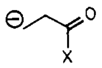
Ed Ehlinger and Philip Magnus*

Contribution from the Evans Chemistry Laboratory, The Ohio State University, Columbus, Ohio 43210. *Received January 1, 1980*

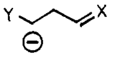
Abstract: The (trimethylsilyl)allyl anion reacts with a number of ketones and aldehydes to give adducts **11–21**, resulting from the γ mode of ambident reactivity. These adducts were epoxidized to provide the corresponding α,β-epoxysilanes **23–31**. Treatment of the epoxysilanes with methanol in the presence of boron trifluoride etherate gave the lactol methyl ethers **32–39**. Jones oxidation of the lactol methyl ethers gave γ lactones **40–45**. Addition of bromine to the 4-hydroxy vinylsilane derivative **19** gave the oxetane **47** which was converted into the compounds **49**, **50**, and **51**. Application of the (trimethylsilyl)allyl anion, as its zinc counterion, to the synthesis of 17-spirosteroidal lactones is described.

Introduction

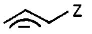
As an extension of classical enolate anion chemistry, the concept of umpolung[1] or reverse polarity has received much ingenious attention during the past several years. The β-acyl anion **1** or homoenolate is a particularly important synthetic species since it is capable of converting aldehydes or ketones into γ-lactols or γ-lactones, depending upon the nature of X. In most attempts to produce reagents that behave as overall equivalents to **1**, the carbonyl group is masked, although some efforts have been made to have direct access to **1**.[2]



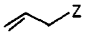
1



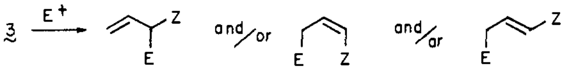
2



3



4



5 5a 5b

---

[1] For a review describing methods of reactivity for umpolung, see: Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239 For nucleophilic acylation, see: Lever, O. W., Jr. *Tetrahedron* **1976**, *32*, 1943. Martin, S. F. *Synthesis* **1979**, 633.

0002-7863/80/1502-5004$01.00/0