compared to some of current interest.[7] These results may also be relevant to puzzling differences reported between Ar matrix and organic glass photochemistry, as in the case of phenyl azide.[32,33]

Acknowledgment. We thank the National Science Foundation (CHE-8421290 and CHE-8709100), the Alfred P. Sloan Foundation, and the Petroleum Research Fund, administered by the American Chemical Society, for support. We also thank David Birney for communication of unpublished results.

Supplementary Material Available: Spectral data for azo compounds **1**, **5**, **6**, and **7** and the corresponding norbornadienones (2 pages). Ordering information is given on any current masthead page.

---

(32) Leyva, E.; Platz, M. S.; Persey, G.; Wirz, J. *J. Am. Chem. Soc.* **1986**, *108*, 3783.

(33) Chapman, O. L.; LeRoux, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 282.

Counterattack Reagent Hexamethyldisilane in the Direct Conversion of Aldehydes, Ketones, and Allyl Alcohols to Allyltrimethylsilanes

Jih Ru Hwu*,†

The Department of Chemistry
Johns Hopkins University
Baltimore, Maryland 21218

Lung Ching Lin* and Ben Ruey Liaw

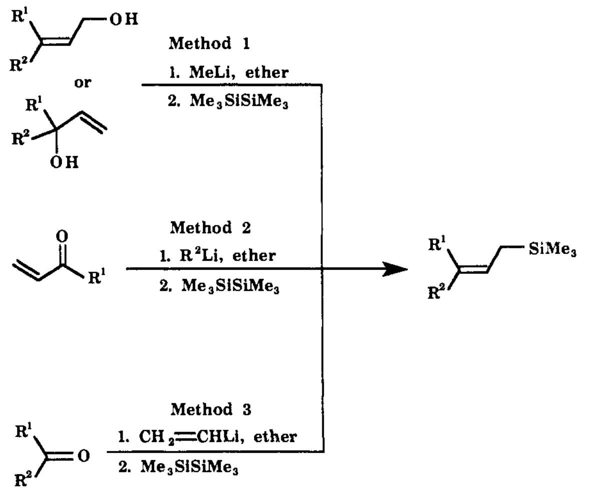
Department of Chemistry
National Taiwan University
Taipei, Taiwan, Republic of China

Received May 31, 1988

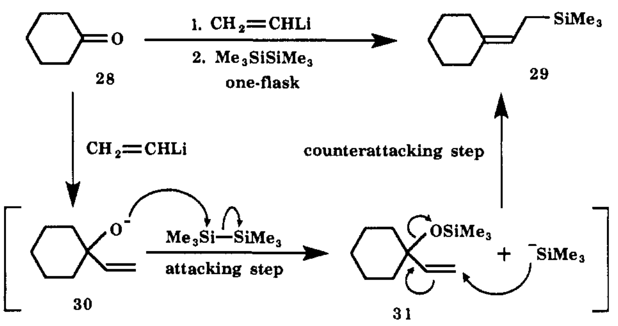
Counterattack reagent[1] Me$_3$SiSiMe$_3$ can efficiently silylate hydrazines under alkaline conditions.[2] We intended to use the counterattack method to prepare another important class of compounds—allyltrimethylsilanes. The allyltrimethylsilane moiety is versatile in organic synthesis.[3-8] This moiety possesses umpolung character and is regarded as a synthon for allyl cations and anions. Three new methods reported herein (see Scheme I) involve the use of Me$_3$SiSiMe$_3$ as a counterattack reagent; allyl alcohols, enals, enones, aldehydes, and ketones can be converted to allyltrimethylsilanes[9] in one flask.

We treated an ether solution of allyl alcohols (1.0 equiv) with MeLi (1.5 equiv) at 0 °C and then added Me$_3$SiSiMe$_3$ (1.5 equiv) and hexamethylphosphoramide (HMPA, ether/HMPA = 1:4).

Scheme I



Scheme II



After ether was boiled off in situ under nitrogen, the reaction mixture was heated at 80 °C for 24 h. Aqueous workup followed by distillation provided the desired allylsilanes[10] (Table I and Scheme I, method 1). Under these conditions, geraniol (**1**) gave allylsilanes **2** and **3**[9a] in 72% yield; linalool (**4**) afforded the same products (**2** and **3**) in 75% yield as well as a small amount of silyl ether **5** (5%); (−)-myrtenol (**6**) provided allylsilane **7** (65%) and silyl ether **8** (15%). When benzyl alcohol (**9**) was used as the starting material, the corresponding trimethylsilane **10**[11] was obtained in only 30% yield. However we were able to convert a homobenzylic compound, phenylethyl alcohol (**12**), to (phenylethyl)silane **13** in 50% yield.

Method 2 in Scheme I illustrates a new method for the preparation of allyltrimethylsilanes[10] from enals and enones by use of alkyllithium and Me$_3$SiSiMe$_3$. We treated acrolein (**14**, 1.0 equiv) sequentially with *n*-BuLi (1.2 equiv) and Me$_3$SiSiMe$_3$ (1.2 equiv) to give allylsilanes **15** and **16**[12] in 48% yield (**15**/**16** = 5:1) as well as *sec*-silyl ether **17** in 10% yield. By use of the same procedure, methyl vinyl ketone (**18**) afforded allylsilanes **19**[9b] and **20** in 48% yield (**19**/**20** = 3:1).

We found that the reaction of saturated aldehydes or ketones with vinyllithium (1.3 equiv) and Me$_3$SiSiMe$_3$ (1.3 equiv) also produced allyltrimethylsilanes[10] (Table I and Scheme I, method 3). Thus 1-hexanal (**21**) gave allylsilanes **22** and **23** in 48% yield (**22**/**23** = 5:1); 2-heptanone (**25**) afforded allylsilanes **26** and **27** in 66% yield (**26**/**27** = 2:1); cyclohexanone (**28**) led to allylsilanes **29** in 75% yield.[13]

For the preparation of allyltrimethylsilanes by methods 1–3, the first step was to generate an allyl alkoxide: removal of the

---

† Research fellow of the Alfred P. Sloan Foundation (1986–1990).

(1) For the definition, see: Hwu, J. R.; Gilbert, B. A. *Tetrahedron* **1989**, in press.

(2) Hwu, J. R.; Wang, N. *Tetrahedron* **1988**, *44*, 4181.

(3) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200.

(4) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlag, 1983; Chapter 11.

(5) Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1.

(6) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: Boston, 1981; Chapter 9.

(7) Calas, R. *J. Organomet. Chem.* **1980**, *200*, 11.

(8) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761.

(9) For recent reports on the preparation of allyltrimethylsilanes, see: (a) Biran, C.; Dunoguès, J.; Calas, R.; Gerval, J.; Tskhovrebachvili, T. *Synthesis* **1981**, 220. (b) Negishi, E.; Luo, F.-T.; Rand, C. L. *Tetrahedron Lett.* **1982**, *23*, 27. (c) Smith, J. G.; Quinn, N. R.; Viswanathan, M. *Synth. Commun.* **1983**, *13*, 1. (d) Smith, J. G.; Quinn, N. R.; Viswanathan, M. *Synth. Commun.* **1983**, *13*, 773. (e) Smith, J. G.; Drozda, S. E.; Petraglia, S. P.; Quinn, N. R.; Rice, E. M.; Taylor, B. S.; Viswanathan, M. *J. Org. Chem.* **1984**, *49*, 4112. (f) Shiragami, H.; Kawamoto, T.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1986**, *27*, 589. (g) Wang, K. K.; Dhumrongvaraporn, S. *Tetrahedron Lett.* **1987**, *28*, 1007. (h) Anderson, M. B.; Fuchs, P. L. *Synth. Commun.* **1987**, *17*, 621. (i) Narayanan, B. A.; Bunnelle, W. H. *Tetrahedron Lett.* **1987**, *28*, 6261.

(10) All compounds were fully characterized by ^{1}H NMR, ^{13}C NMR, IR, and high resolution mass spectroscopy; the experimental and physical characteristics of each compound are available as Supplementary Material.

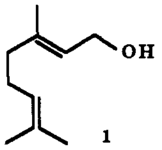
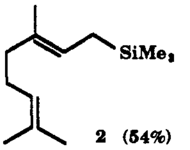
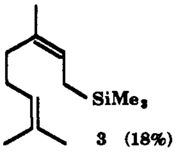
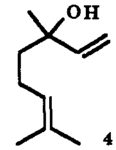
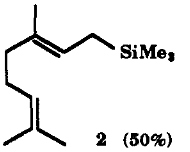
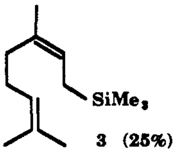
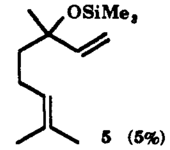
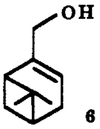
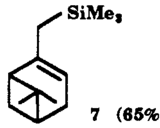
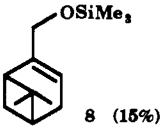
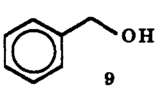
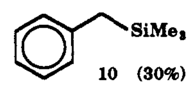
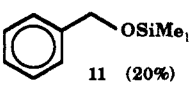
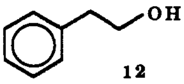
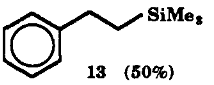
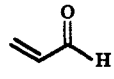
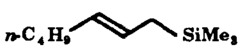
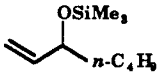
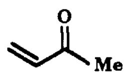
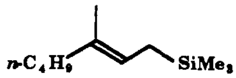
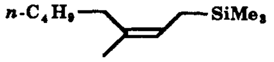
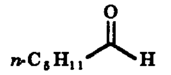
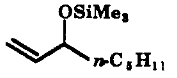
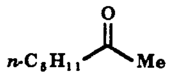
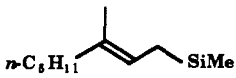
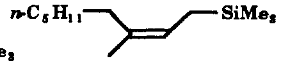
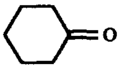
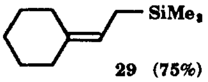
(11) Pons, P.; Biran, C.; Bordeau, M.; Dunogues, J.; Sibille, S.; Perichon, J. *J. Organomet. Chem.* **1987**, *321*, C27.

(12) Rajagopalan, S.; Zweifel, G. *Synthesis* **1984**, 113.

(13) For a previous transformation of **28** to **29**, see: (a) Seyferth, D.; Wursthorn, K. R.; Mammarella, R. E. *J. Org. Chem.* **1977**, *42*, 3104. (b) Fleming, I.; Paterson, I. *Synthesis* **1979**, 446.

0002-7863/88/1510-7252$01.50/0

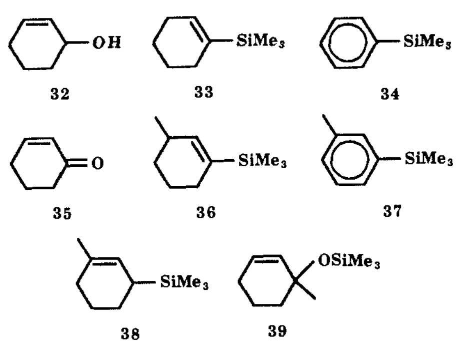
Table I. Allyltrimethylsilanes from Alcohols and Carbonyl Compounds by Methods 1-3 in Scheme I

starting material	allyltrimethylsilane	byproduct
 **1**	 **2** (54%)  **3** (18%)	
 **4**	 **2** (50%)  **3** (25%)	 **5** (5%)
 **6**	 **7** (65%)	 **8** (15%)
 **9**	 **10** (30%)	 **11** (20%)
 **12**	 **13** (50%)	
 **14**	 **15** (40%)  **16** (8%)	 **17** (10%)
 **18**	 **19** (36%)  **20** (12%)	
 **21**	 **22** (40%)  **23** (8%)	 **24** (15%)
 **25**	 **26** (44%)  **27** (22%)	
 **28**	 **29** (75%)	

proton from an allyl alcohol with MeLi in method 1; 1,2-addition of RLi to an α,β-unsaturated aldehyde or ketone in method 2; or addition of vinyllithium to a saturated carbonyl compound in method 3. The allyl alkoxide then reacted with $Me_3SiSiMe_3$ by a novel pathway to give allyltrimethylsilanes in situ; Scheme II shows a proposed mechanism with cyclohexanone and vinyllithium as the starting material.

Hexamethyldisilane was attacked by allyl alkoxide **30**, generated by addition of vinyllithium to ketone **28**, to give allyl trimethylsilyl ether **31** and Me_3Si^-.[14] Leaving group Me_3Si^- then counterattacked intermediate **31** by an S_N2' pathway to produce the corresponding allyltrimethylsilane **29** and Me_3SiO^-. In the counterattacking step (i.e., **31** → **29**), a strong C–O bond (86 kcal/mol) in **31** was cleaved and a weak Si–C bond (72 kcal/mol) in **29** was formed.[15] However highly unstable species Me_3Si^- was consumed and more stable anion Me_3SiO^- was generated. Therefore conversion of **31** to **29** was a thermodynamically favorable process.

Chart I



In the entire pathway shown in Scheme II, $Me_3SiSiMe_3$ behaved as a counterattack reagent.

Each of the methods 1–3 involved an allyl trimethylsilyl ether as the intermediate. In the reactions with **4**, **6**, **9**, **14**, and **21** as the starting material, we were able to detect silyl ethers **5**, **8**, **11**, **17**, and **24**, respectively, in the crude reaction products.

We attempted to prepare a cyclic allyltrimethylsilane from a cyclic allyl alcohol (**32**) by method 1 after having had success in primary allyltrimethylsilanes. Nevertheless we obtained only

---

[14] (a) Sakurai, H.; Okada, A.; Kira, M.; Yonezawa, K. *Tetrahedron Lett.* **1971**, 1511. (b) Sakurai, H.; Okada, A. *J. Organomet. Chem.* **1972**, *35*, C13. (c) Sakurai, H.; Kondo, F. *J. Organomet. Chem.* **1975**, *92*, C46. (d) Shippey, M. A.; Dervan, P. B. *J. Org. Chem.* **1977**, *42*, 2654.

[15] Sommer, L. H. *Stereochemistry, Mechanism, and Silicon*; McGraw-Hill: New York, 1965; p 24.

vinyltrimethylsilane **33** (65%) and aromatized product **34** (7%). When employing the conditions of method 2 (R^2Li = MeLi) to 2-cyclohexen-1-one (**35**), we also isolated the corresponding vinyltrimethylsilane **36** as the major product (36%). The desired allyltrimethylsilane **38** was obtained in 15% yield; other minor products included aromatic silane **37** (15%) and trimethylsilyl ether **39** (5%).

In conclusion, use of the counterattack method facilitated the preparation of allyltrimethylsilanes. Treatment of the readily available starting material, allyl alcohols, enals, enones, aldehydes, or ketones with organolithium reagents gave allyl alkoxides. The alkoxides then reacted with $Me_3SiSiMe_3$ to afford trimethylsilyl ethers and Me_3Si^-. In situ a substitution reaction occurred between these two species to produce allyltrimethylsilanes in good yields. In these one-flask reactions, $Me_3SiSiMe_3$ behaved as a counterattack reagent.

Acknowledgment. Hwu is grateful for financial support provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society; the American Heart Association, the Maryland Affiliate, Inc.; the American Cancer Society Institutional Research Grant IN-11Z; and the Biomedical Research Support Grant S07 RR7041 awarded by the National Institutes of Health. A grant from the National Institutes of Health for supporting the purchase of a VG 70-S mass spectrometer is also acknowledged. Lin and Liaw thank the National Science Council of the Republic of China for a research grant.

Electronic Properties and Redox Conduction of Ferrocene-Substituted High Polymeric Phosphazenes

Reginaldo A. Saraceno, Geoffrey H. Riding,
Harry R. Allcock,* and Andrew G. Ewing*

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

Received June 29, 1988
Revised Manuscript Received September 2, 1988

We have recently reported on the electronic properties of phosphazene substituents which affect thermodynamic shifts in the oxidation peak potential of ferrocene.[1] Examination of the electrochemistry of ferrocene bonded to phosphazenes provides a direct probe of the electronic and bonding structure of this important class of molecules. In this paper we present the first thermodynamic and kinetic data obtained for the electrochemical oxidation and reduction of ferrocene-substituted polyphosphazenes $[N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe]_n$ (I), $[N_3P_3(OCH_2CF_3)_5(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]_n$ (II), and $[N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe]_n$ (III).

Cyclic voltammetry and chronoamperometry at platinum disk electrodes (radius = 1.9 mm) coated with evaporatively deposited (from DMF) polymers were used to study electron transfer and cross exchange processes. Voltammograms for a surface immobilized film of I in dichloromethane are shown in Figure 1A. Voltammetry of I in acetonitrile solutions results in irreproducible electrochemistry and deterioration of the polymer film apparently due to a chemical reaction of oxidized I with acetonitrile. Electrochemistry in dichloromethane is reproducible and can be used to ascertain the thermodynamic properties of this polymer. The surface coverage of the polymer (Γ) was obtained by integrating the area under the oxidation wave.[2]

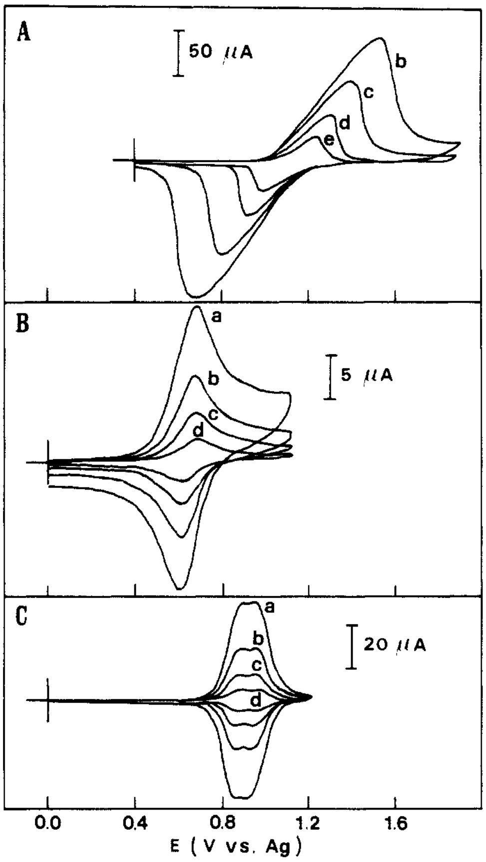


Figure 1. Cyclic voltammograms of evaporatively deposited polyphosphazenes I (A), II (B), and III (C), on Pt electrodes, in 0.1 M tetrahexylammonium perchlorate/dichloromethane (A) or 0.1 M tetraethylammonium perchlorate/acetonitrile (B and C). Scan rates: 0.2 (a), 0.1 (b), 0.05 (c), 0.02 (d), 0.01 (e) V/s. Surface coverage $\Gamma = 4.9 \times 10^{-8}$ mol/cm^2 (A), 1.6×10^{-9} mol/cm^2 (B), and 4.8×10^{-9} mol/cm^2 (C).

Table I. Charge Transport Rates of Ferrocene-Substituted Polyphosphazenes[a]

compd	$(D_{ct}^{1/2}C)_{anod}$[b,c] (10^{-8} mol/cm^2)	$(D_{ct}^{1/2}C)_{cath}$[c] (10^{-8} mol/cm^2)
I[d]	1.41 (±0.15)	1.52 (±0.24)
II	1.96 (±0.18)	1.81 (±0.44)
III	3.20 (±0.20)[e]	6.19 (±1.65)
III	7.49 (±0.71)[f]	

[a] The preanalysis potential was held at either 0.0 or 1.0 V for II and 1.3 V for III for at least 60 s prior to the application of the forward (oxidation) or reverse (reduction) potential step, respectively, to assure a homogeneous film oxidation state and to eliminate effects from insufficient film oxidation or reduction as an initial condition. [b] $n = 18$ for all averages except I ($n = 5$) and $(D_{ct}^{1/2}C)_{anod}$ for II ($n = 21$). [c] Values in parentheses represent the 95% confidence interval. [d] Values for this polymer calculated with the Randles–Sevcik equation. [e] Values obtained between 10 and 25 ms. [f] Values obtained between 25 and 50 ms.

The large difference between oxidation and reduction peak potentials (ΔE_p) and asymmetrical peak shapes are typical of the voltammetry obtained with platinum electrodes modified with polymer films of I. The separation between voltammetric peaks ranges from a low of 0.26 V at a 10 mV/s scan rate to a high of 1.24 V at a 200 mV/s scan rate. Plots of $(i_p)_{anod}$ versus square root of scan rate ($v^{1/2}$) were linear (correlation coefficient = 0.9965, $n = 5$) for values between the scan rate limits examined.

The linear relationship between $(i_p)_{anod}$ and $v^{1/2}$ indicates that charge transfer is similar to a semi-infinite linear diffusion process as described by the Randles–Sevcik equation.[3] Rates for charge transport ($D_{ct}^{1/2}C$) for I are listed in Table I. The large variation of peak potentials with scan rate suggests that the polymer film undergoes a chemical reaction following the oxidation of ferrocene. This result is similar to the voltammetry observed for its low molecular weight analogue $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$.[1] The oxidized and chemically rearranged phosphazenyl ferrocene is reduced at

---

(1) Saraceno, R. A.; Riding, G. H.; Allcock, H. R.; Ewing, A. G. *J. Am. Chem. Soc.* **1988**, *110*, 980–982.

(2) Murray, R. W. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1984; Vol. 13.

(3) Randles-Sevcik equation: $i_p = (2.69 \times 10^5)n^{3/2}AD^{1/2}Cv^{1/2}$, ref 9, p 218.

0002-7863/88/1510-7254$01.50/0