J. Org. Chem. **1992**, *57*, 2427–2433

tained from the reaction of 2-bromo-3,5-dimethoxybenzaldehyde and methyl acrylate followed by recrystallization (EtOAc–hexane) gave colorless needles of **2I** (57%): mp 103–105 °C; IR (Nujol) 1731, 1686, 1619 cm^{-1}; ^{1}H NMR (80 MHz) δ 3.79 (s, 3 H, CO_2Me), 3.81 and 3.99 (s, 3 H each, OMe), 6.39 and 8.15 (d, 1 H each, J = 15.9 Hz, alkene H), 6.7 and 7.1 (d, 1 H each, J = 2.5 Hz, aromatic H), 10.1 (s, 1 H, CHO); HRMS (EI) m/z 250.0884, calcd for $C_{13}H_{14}O_5$, M$^+$, 250.0881. Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.40; H, 5.60. Found: C, 62.46; H, 5.64.

Methyl 3-(3′-Formylphenyl)-2-propenoate (2J). Flash chromatography (EtOAc–hexane, 1:5) of the oil obtained from the reaction of *m*-bromobenzaldehyde and methyl acrylate followed by recrystallization (EtOAc–hexane) gave colorless needles of **2J** (63%); mp 55–56 °C; IR (Nujol) 1740, 1680, 1617 cm^{-1}; ^{1}H NMR (80 MHz) δ 3.81 (s, 3 H, CO_2Me), 3.86 (s, 3 H, OMe), 6.54 (d, 1 H, J = 15.9 Hz, alkene H), 7.55–8.03 (m 5 H, aromatic H + alkene H), 10.04 (s, 1 H, CHO); HRMS (EI) m/z 190.0630, calcd for $C_{11}H_{10}O_3$, M$^+$, 190.0630.

Methyl 3-[2′-(2-Carbomethoxyethyl)-4′-methoxy-5′-nitrophenyl]-2-propenoate (4). The title compound was prepared from 2-bromo-4-methoxy-5-nitrobenzaldehyde according to the general procedure (29%): mp 114–115 °C (CH_2Cl_2–hexane–ether); IR (Nujol) 1730, 1716, 1620 cm^{-1}; ^{1}H NMR (200 MHz) δ 2.62, 3.14 (t, 2 H each, J = 7.4 Hz, CH_2), 3.68, 3.82, (s, 3 H each, CO_2Me), 3.98 (s, 3 H, OMe), 6.37, 7.83 (d, 1 H each, J = 15.7 Hz, alkene H), 6.98, 8.10 (s, 1 H each, aromatic H); HRMS (EI) m/z 323.1003, calcd for $C_{15}H_{17}O_7N$, M$^+$, 323.1005. Anal. Calcd for $C_{15}H_{17}O_7N$: C, 55.38; H, 5.26. Found: C, 55.30; H, 5.21.

Crystal Structure Analysis of 4. Crystals of $C_{15}H_{17}NO_7$, M = 323.3 are triclinic, space group $P\bar{1}$, a = 7.820 (2), b = 9.418 (2), and c = 11.337 (2) Å, α = 99.83 (1)°, β = 100.97 (1)°, γ = 100.87 (1)°, V = 786.3 (2) Å^3, with Z = 2, D_c = 1.365 g cm^{-3}, $F(000)$ = 340, λ = 0.71073 Å, T = 295 K, μ (Mo Kα) = 1.02 cm^{-1}. Data were collected on a Siemens R3m/V diffractometer from a crystal of dimensions 0.48 ($100, \bar{1}00$) × 0.32 ($010, 0\bar{1}0$) × 0.36 ($\bar{1}11, 1\bar{1}\bar{1}$) mm. From 3105 independent data measured by the ω scan method, ($2\theta \leq 52°$), 1863 (with $F \geq 6\sigma(F)$) were considered observed and used in the structure solution and refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods to R and R_w values of 6.15 and 8.02% (Siemens SHELXTL PLUS software). Full details of the X-ray analysis are listed in the supplemental data. In the molecular plot (Figure 1), one of the side chains is illustrated as disordered at C(12) and C(13) such that the methylene unit C(13) occupies two distinct sites and four proton positions were located in a difference map associated with the methylene carbon C(12). The disorder was estimated to be 65:35. The remainder of the side chain appears quite ordered.

Acknowledgment. We thank the Natural Science and Engineering Research Council of Canada for support of this work.

Supplementary Material Available: ^{1}H NMR spectra of **5**, **7**, **10**, and **13** and X-ray crystallographic data for **4** (14 pages). Ordering information is given on any current masthead page.

A Study on the Reducing Abilities of Tris(alkylthio)silanes[1]

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Received October 8, 1991

Tris(methylthio)silane and tris(isopropylthio)silane effectively reduce a variety of organic substrates via free radical mechanisms. These silanes can also be used as hydrosilylating agents for alkenes having electron-donating substituents. The bond dissociation energy of the Si–H bonds have been measured by photoacoustic calorimetry and found to be around 83 kcal mol^{-1}. The absolute rate constants for the reaction of the *tert*-butoxyl radical with $(RS)_3SiH$ have been measured by a laser flash photolysis technique and the optical absorption spectra of the corresponding radicals have been obtained. Multiple scattering X_α calculations showed that the dominant absorption detected in the UV–vis region was due to $\sigma_{Si-S}(e) \rightarrow$ SOMO and SOMO $\rightarrow \sigma^*_{Si-S}(e)$ transitions.

Introduction

In organic synthesis, the most useful types of free radical reactions are (i) reductions of a variety of functional groups and (ii) the formation of carbon–carbon bonds, either inter- or intramolecularly.[4] Such chain processes have been carried out by using tri-*n*-butyltin hydride[5] and, more recently, tris(trimethylsilyl)silane.[6-8] One of the most important considerations in selecting different reducing agents for these processes concerns the relative hydrogen–donor abilities of the hydrides,[9] viz., eq 1.

$$R^\bullet + X_3MH \rightarrow RH + X_3M^\bullet \qquad (1)$$

Trialkylgermanium hydrides are less reactive donors than their tin analogues, while the corresponding germyl radicals are at least as reactive as stannyl radicals in reactions with organic substrates.[12] However, due mainly to the high cost

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[4] Giese, B. *Angew. Chem., Int. Ed. Engl.* **1989**, *24*, 969. Curran, D. P. *Synthesis* **1988**, 417, 489. Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, 1986.

[5] Neumann, W. P. *Synthesis* **1987**, 665 and references cited therein.

[6] Ballestri, M.; Chatgilialoglu, C.; Clark, K. B.; Griller, D.; Giese, B.; Kopping, B. *J. Org. Chem.* **1991**, *56*, 678. Lesage, M.; Chatgilialoglu, C.; Griller, D. *Tetrahedron Lett.* **1989**, *30*, 2733. Chatgilialoglu, C.; Griller, D.; Lesage, M. *J. Org. Chem.* **1988**, *53*, 3641.

[7] Chatgilialoglu, C.; Giese, B.; Kopping, B. *Tetrahedron Lett.* **1990**, *31*, 6013. Giese, B.; Kopping, B.; Chatgilialoglu, C. *Tetrahedron Lett.* **1989**, *30*, 681.

[8] Arya, P.; Samson, C.; Lesage, M.; Griller, D. *J. Org. Chem.* **1990**, *55*, 6248. Schummer, D.; Höfle, G. *Synlett* **1990**, 705. Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. Cs. *Tetrahedron Lett.* **1990**, *31*, 4681. Hitchcock, S. A.; Pattenden, G. *Tetrahedron Lett.* **1990**, *31*, 3641.

[9] For example, rate constants for reaction 1, where R$^\bullet$ = primary, secondary, and tertiary alkyl radicals, are 2.3×10^6, 1.5×10^6, and 1.9×10^6 M^{-1} s^{-1} for Bu_3SnH[10] and 3.7×10^5, 1.4×10^5, and 2.6×10^5 M^{-1} s^{-1} for $(Me_3Si)_3SiH$,[11] respectively, at 298 K.

[10] Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739.

[11] Chatgilialoglu, C.; Dickhaut, J.; Giese, B. *J. Org. Chem.* **1991**, *56*, 6399.

[12] Lusztyk, J.; Maillard, B.; Deycard, S.; Linday, D. A.; Ingold, K. U. *J. Org. Chem.* **1987**, *52*, 3509.

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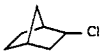
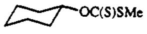
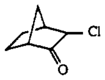
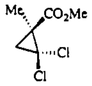
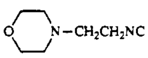
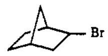
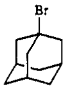
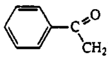
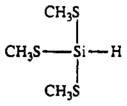
Table I. Reduction of Some Organic Compounds by Tris(alkylthio)silanes

RZ	$(MeS)_3SiH$ yield,[a] %	$(i\text{-}PrS)_3SiH$ yield,[a] %	RZ	$(MeS)_3SiH$ yield,[a] %	$(i\text{-}PrS)_3SiH$ yield,[a] %
	b	b		97	98
	65	67		98	99
		64		b	b
$CH_3(CH_2)_{14}CH_2Br$	94	96		71	73
	98	96		96	79
	98	96	Me_3SiCH_2NC		95
	94	98	$Me_3COC(O)CH_2NC$		70
$CH_3(CH_2)_{14}CH_2I$	97	98			

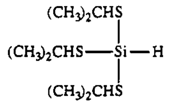
[a] Yields are based on the formation of corresponding hydrocarbon and on the amount of substrate converted. Conversions and yields were quantified by GC using decane as an internal standard. Conversions, which are based on disappearance of the starting material, are larger than 80% and in most cases complete. [b] Under normal conditions, conversions are less than 30%.

of germanium hydrides, tin hydrides have been used in low concentrations to achieve similar results.[4] In our continued exploration of the use of organosilanes as radical-based reducing agents, some of us recently reported preliminary work on the use of tris(alkylthio)silanes as new reducing agents.[13] On the basis of a correlation[14] between bond dissociation energies of trisubstituted silanes, i.e., BDE(Y_3Si–H), and the sum of substituent group electronegativities, i.e. $\sum\chi_Y$, a bond strength of 82–83 kcal mol^{-1} is predicted for $(MeS)_3Si$–H. This value is similar to the BDE of trialkylgermanium hydrides.[15] These results suggest that tris(alkylthio)silanes could be attractive alternatives to trialkylgermanium hydrides for a variety of radical chain reactions. In the present work, we have extended the use of 1 and 2 as radical reducing agents. We have also employed photoacoustic and optical absorption techniques, together with ab initio and Multiple Scattering X_α calculations, to measure Si–H bond dissociation energies and to study mechanistic and structural aspects of related radicals.



$(CH_3S)_3Si{-}H$

1



$((CH_3)_2CHS)_3Si{-}H$

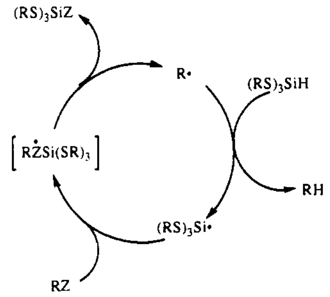
2

Results and Discussion

General Remarks. Compounds 1 and 2 were prepared in yields of 40% and 65%, respectively, using trichlorosilane, pyridine, and alkanethiols (eq 2).[16] A mixture of

$$3RSH + Cl_3SiH \xrightarrow{\text{pyridine}} (RS)_3SiH \qquad (2)$$

Scheme I



tris(methylthio)silane (0.3 M) in toluene as a solvent was heated at 80 °C for 2 h. Analysis by GC/MS revealed the absence of new products.[17] When a radical initiator was introduced, i.e., AIBN (azobis(isobutyronitrile)), as reaction occurred. That is, the starting material was consumed (ca. 30% in 2 h), forming tetrakis(methylthio)silane as the major product and a number of undentified minor products. In view of the affinity of silyl radicals for sulfur-containing substrates,[18] we believe that eq 3 is the key step in the formation of tetrakis(methylthio)silane. Tris(isopropylthio)silane behaved similarly. That is, the starting

$$(MeS)_3Si^{\bullet} + (MeS)_3SiH \rightarrow (MeS)_4Si + (MeS)_2\dot{S}iH \qquad (3)$$

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[13] Chatgilialoglu, C.; Guerrini, A.; Seconi, G. *Synlett* **1990**, 219. Ballestri, M.; Chatgilialoglu, C.; Dembech, P.; Guerrini, A.; Seconi, G. In *Sulfur-Centered Reactive Intermediates in Chemistry and Biology*; Chatgilialoglu, C., Asmus, K.-D., Eds.; Plenum Press: New York, 1990; pp 319–325.

[14] Chatgilialoglu, C. In *Free Radicals in Synthesis and Biology*; Minisci, F., Ed.; Kluwer: Dordrecht, 1989; pp 115–127.

[15] Clark, K. B.; Griller, D. *Organometallics* **1991**, *10*, 746.

[16] Lambert, J. B.; Schulz, W. J., Jr.; McConnell, J. A.; Schilf, W. *J. Am. Chem. Soc.* **1988**, *110*, 2201. Wolinski, L.; Tieckelmann, H.; Post, H. W. *J. Org. Chem.* **1951**, *16*, 395.

[17] Traces of alkanethiols always are present in the GC runs of tris(alkylthio)silanes. We believe that such amounts of alkanethiols are formed from the decomposition of corresponding silanes at ca. 250 °C.

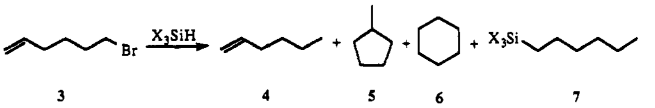
[18] The bond dissociation energy of Si–S in Me_3SiSBu is estimated to be 99 kcal mol^{-1}: Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

[19] Roberts and his co-workers[20] recently reported that trialkylsilanes reduce alkyl halides and xanthates to the corresponding hydrocarbons in the presence of alkanethiols, which act as polarity reversal catalysts for hydrogen transfer from the silane to the alkyl radical. Thus, any traces of alkanethiols that may be formed during our experiments could be take part in the reaction as catalyst. Although we cannot exclude such a possibility, based on the observed quantities of alkanethiols[17] and on the available kinetic data,[21] we are confident that such an alternative reaction scheme is either unimportant or does not occur at all.

[20] Cole, S. J.; Kirwan, J. N.; Roberts, B. P.; Willis, C. R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 103–112. Allen, R. P.; Roberts, B. P.; Willis, C. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1387. Kirwan, J. N.; Roberts, B. P.; Willis, C. R. *Tetrahedron Lett.* **1990**, *31*, 5093.

[21] Newcomb, M.; Glenn, A. G.; Manek, M. R. *J. Org. Chem.* **1989**, *54*, 4603.

Scheme II



	4	5	6	7
$(MeS)_3SiH$	4.7%	62%	1.3%	25%
$(i\text{-}PrS)_3SiH$	6.7%	78%	1.5%	15%
$(Me_3Si)_3SiH$	7.9%	86%	1.8%	

material was consumed in 2.5 h (in the presence of AIBN), forming tetrakis(isopropylthio)silane in 10% yield and a major product of higher molecular weight, which has not yet fully characterized. Further work on free radical initiated decompositions of tris(alkylthio)silanes are currently under investigation in our laboratories and we hope soon to be able to give more information on these reactions.

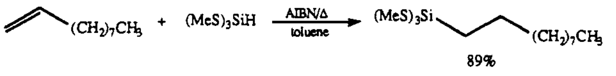
Reduction of Organic Derivatives. Reductions of a variety of organic derivatives were carried out by using tris(alkylthio)silanes. Reactions of each derivative with either **1** or **2** at 75–90 °C in toluene and in the presence of a radical initiator, i.e., AIBN, gave the corresponding hydrocarbons in good yields (see Table I). Sample analyses were carried out using GC and authentic samples as calibrants. Yields were quantified by using an internal standard.

Evidence for a free radical chain mechanism (Scheme I) was provided by the observations that the reactions were catalyzed by light and by thermal sources of free radicals such as AIBN and dibenzoyl peroxide.[19] Furthermore the reactions were retarded by 2,6-*tert*-butyl-4-methylphenol and duroquinone, which are expected to be inhibitors of the two propagation steps, respectively. Structure $[R\dot{Z}Si(SR)_3]$ represents a reactive intermediate or a transition state (cf. ref 6).

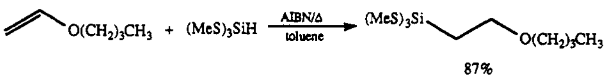
Reductions of bromides and iodides were straightforward and the reactions were complete after a short time (ca. 0.5 h). Secondary alkyl xanthates and selenides were also reduced by the silane, as expected in view of the affinity of silyl radicals for sulfur- and selenium-containing substrates. Primary, secondary, and tertiary isocyanides gave the corresponding hydrocarbon in good yields (Table I). For chlorides and sulfides the reductions were difficult due to the shorter chain lengths. Therefore, a longer reaction time and periodic addition of initiator was necessary. However, the reduction of chlorides is facilitated when α-stabilizing groups or *gem*-dichlorides are present.

Reaction of 5-hexenyl bromide (**3**) (0.33 M) with silanes **1** and **2** in toluene at 75 °C containing catalytic amounts of AIBN afforded the expected products[22] **4**, **5**, and **6** in ratio of ca. 4:50:1 together with the unexpected hydrosilylated product **7** (Scheme II). On the other hand, the corresponding hydrosilylated product in the reaction with $(Me_3Si)_3SiH$ is absent, under the same experimental conditions. This observation indicates that the gap between the rate constants for addition and bromine abstraction of $(Me_3Si)_3Si^\bullet$ and $(RS)_3Si^\bullet$ is rather large.[23] A possible explanation for this behavior could be the different nucleophilicity of the two radicals (vide infra).

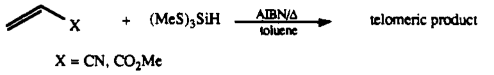
Hydrosilylation of Olefins. It is well-known that trialkylsilyl radicals are among the most reactive species known for addition to double bonds.[24] However, free radical hydrosilylations using trialkylsilanes are impractical processes under normal conditions, due probably to the high Si–H bond energy. On the other hand, tris(trimethylsilyl)silane is capable of substaining radical hydrosilylation of olefins in very good yields,[26] because its Si–H bond energy is low enough. Therefore, it is expected that tris(alkylthio)silanes are also good hydrosilylation agents. This expectation turned out to be only partially correct. That is, the success of hydrosilylation depends upon the electronegativity of the olefin substituents. Thus, electron-donating groups such as alkyl (eq 4) or alkoxyl (eq 5) give good yields of hydrosilylation products whereas electron-withdrawing groups give only telomeric material (eq 6). We believe that "polar effects" in the transition states of both propagation steps play an important role,[27] indicating also that the $(MeS)_3Si^\bullet$ radical is more electrophilic in character than the $(Me_3Si)_3Si^\bullet$ radical.



(4)

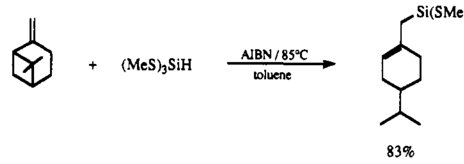


(5)



(6)

The hydrosilylation of β-pinene was performed in order to gain further knowledge about the reaction mechanism. The addition of $(MeS)_3SiH$ to β-pinene in a toluene solution affords an 83% yield of a 1:1 adduct of the two reagents whose NMR spectrum shows the compound to be 7-[tris(methylthio)silyl]-Δ^1-*p*-menthene (eq 7). In fact, under our conditions, the addition of a tris(methylthio)silyl radical to β-pinene will give the expected carbon-centered radical which rearranges by opening of the four-membered ring prior to H transfer.[22]



(7)

Kinetics of Reaction with *tert*-Butoxyl and Spectral Properties of the Tris(alkylthio)silyl Radicals. The experiments were carried out by monitoring the transient absorptions produced when the samples were excited with the pulse (337.1 nm, ~8 ns, ~10 mJ) from a nitrogen laser. For example, photolysis of a 0.1 M solution of $(RS)_3SiH$ in 1:4 (v/v) di-*tert*-butyl peroxide/isooctane (or benzene) as solvent results in the formation of transient species which exhibit the spectra shown in Figure 1. These transient species decay with second-order kinetics. Under these conditions, the laser pulses are absorbed exclusively by the peroxide, which undergoes a fast and efficient decomposition to yield *tert*-butoxyl radical (eq 8).[28] We propose that the spectra described above are

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(22) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 1, Essay 4.

(23) Rate constants for the reactions of triethylsilyl radicals with $CH_2{=}CH(CH_2)_3CH_3$[24] and $CH_3(CH_2)_4Br$[25] are 4.8×10^6 and 5.4×10^8 M^{-1} s^{-1}, respectively, at 300 K.

(24) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 3292.

(25) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5123.

(26) Kopping, B.; Chatgilialoglu, C.; Zehnder, M.; Giese, B. *J. Org. Chem.* In press.

(27) For general discussions of polar effects in radical reactions, see: Russell, G. A. *Free Radicals* **1973**, *1*, 275. Minisci, F.; Citterio, A. *Adv. Free-Radical Chem.* **1980**, *6*, 65.

(28) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C.; Woynar, H. *J. Am. Chem. Soc.* **1981**, *103*, 3231.

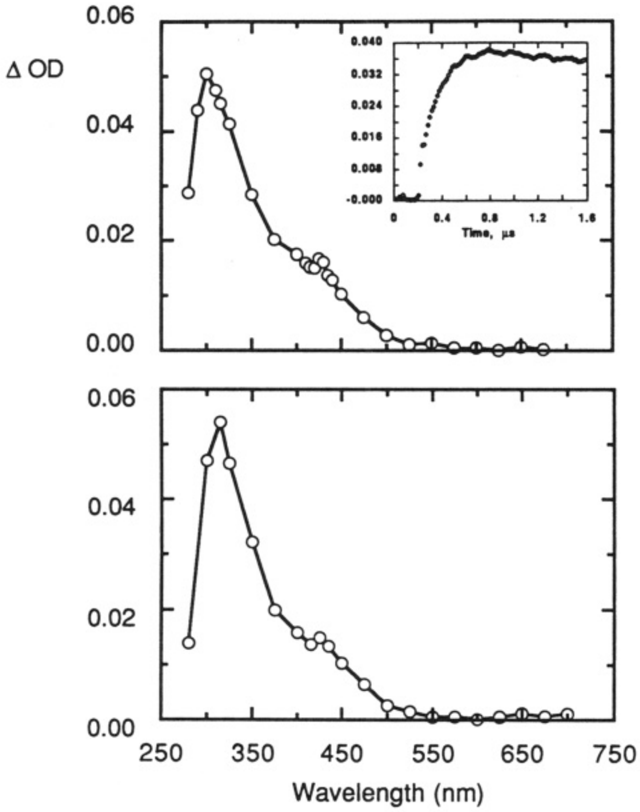


Figure 1. Radical absorption spectra for $(MeS)_3Si^{\bullet}$ (bottom) and $(i\text{-}PrS)_3Si^{\bullet}$ (top) measured 1 μs after 337-nm excitation in 2:1 di-*tert*-butyl peroxide/benzene containing ca. 0.02 M silane. Inset: Growth of the radical absorption monitored at 350 nm.

due to $(MeS)_3Si^{\bullet}$ and $(i\text{-}PrS)_3Si^{\bullet}$ radicals, respectively, generated in reaction 9. A plot of pseudo-first-order rate

$$Me_3COOCMe_3 \xrightarrow{h\nu} 2Me_3CO^{\bullet} \qquad (8)$$

$$2Me_3CO^{\bullet} + 2(RS)_3SiH \rightarrow 2Me_3COH + 2(RS)_3Si^{\bullet} \qquad (9)$$

constants, derived from the buildup of the signals as a function of $[(RS)_3SiH]$, yields k_9 of $(4.4 \pm 0.3) \times 10^7$ and $(4.5 \pm 0.2) \times 10^7$ M^{-1} s^{-1} for $(MeS)_3SiH$ and $(i\text{-}PrS)_3SiH$, respectively, at 298 K.

It should be noticed that the kinetic procedures described yield absolute rate constants but do not distinguish between sites or modes of interaction of tris(alkylthio)silanes with *tert*-butoxyl radicals. Thus, there could be some attack at the methyl and isopropyl groups of silane. However, when tetrakis(alkylthio)silanes replaced tris(alkylthio)silanes, under the same conditions as those described above, no absorption is observed. Rate constants for reaction 10 were also obtained using diphenylmethanol as a probe.[29,30] The k_{10} values of 4.5×10^5 and 1.6×10^5

$$Me_3CO^{\bullet} + (RS)_4Si \rightarrow Me_3COH + [R(-H)S]_4Si \qquad (10)$$

M^{-1} s^{-1} for $(MeS)_4Si$ and $(i\text{-}PrS)_4Si$ at 298 K show that these silanes are significantly less reactive towards *tert*-butoxyl radicals than the corresponding tris(alkylthio)silanes. Therefore, we estimate from these values that >99% of *tert*-butoxyl attack occurs at the Si–H bond of $(MeS)_3SiH$ and $(i\text{-}PrS)_3SiH$.

Comparison of the kinetic data in Table II (column 2) reveals that substitution of alkyl groups by alkylthio or trimethylsilyl groups makes the reaction about 10 and 20 times faster. Apart from effects of electronegativity, the stabilization of $(RS)_3Si^{\bullet}$ and $(Me_3Si)_3Si^{\bullet}$ radicals is probably due to the bonding interaction between the d orbital of the atom next to the radical center and the singly occupied molecular orbital (SOMO) as well as to the hyperconjugation between SOMO and σ^*_{S-C} or σ^*_{Si-C}, respectively.

Table II. Bond Dissociation Enthalpies, DH°(X_3Si–H), and Related Kinetic Data for the Si–H Bonds in Silanes

silane	k_9, M^{-1} s^{-1}	$\Delta H_{8,9}$, kcal mol^{-1}	DH°(X_3Si–H), kcal mol^{-1}
$(MeS)_3SiH$	$(4.4 \pm 0.3) \times 10^7$	-7.2 ± 1.3	82.5
$(i\text{-}PrS)_3SiH$	$(4.5 \pm 0.2) \times 10^7$	-1.0 ± 1.6	85.6
$(Me_3Si)_3SiH$	$(1.1 \pm 0.3) \times 10^{8\,a}$	-14.2^c	79.0^c
Et_3SiH	$(5.7 \pm 0.3) \times 10^{6\,b}$	-8.0^c	90.1^c

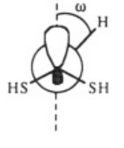
[a] Reference 31. [b] Reference 30. [c] Reference 32.

Table III. Vertical Excitation Energies (nm) for Valence and Rydberg Transitions of the Tris(methylthio)silyl Radical

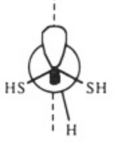
transitions	energy, nm	oscillator strength
$n_S(a_1) \rightarrow$ SOMO	1251	0.000
$n_S(e) \rightarrow$ SOMO	809	0.004
$\sigma_{Si-S}(e) \rightarrow$ SOMO	384	0.095
SOMO $\rightarrow 4s(a_1)$	319	0.000
SOMO $\rightarrow 4p(a_1)$	301	0.024
$\sigma_{Si-S}(a_1) \rightarrow$ SOMO	290	0.022
SOMO $\rightarrow \sigma^*_{Si-S}(e)$	288	0.179
SOMO $\rightarrow \sigma^*_{Si-S}(a_1)$	280	0.052
$\sigma_{Si-S}(e) \rightarrow$ SOMO	272	0.009

In contrast to the $(Me_3Si)_3Si^{\bullet}$ radical, which exhibits a spectrum with continuously increasing absorption below ca. 350 nm and no maximum above 280 nm,[31] the absorption spectra of $(MeS)_3Si^{\bullet}$ and $(i\text{-}PrS)_3Si^{\bullet}$ radicals show a strong band with λ_{max} at 300–310 nm (Figure 1). In addition, the absorption envelopes extend well out into the visible region of the spectrum to about 500 nm and show a shoulder at ca. 425 nm.

The structural parameters for the $(MeS)_3Si^{\bullet}$ radical were determined by optimizing the $(HS)_3Si^{\bullet}$ radical as a model compound at the HF/6-31G* level with the C_3 symmetry constant utilizing the GAUSSIAN86 series of programs. The radical center at silicon is pyramidal. Two minima have been found along the energy surface generated by the synchronous rotation of the SH groups. In the most stable conformation **8**, the hydrogens adopt a gauche conformation ($\omega = 52°$) with respect to the singly occupied molecular orbital (SOMO) which is mainly localized at the sp_3 atomic orbital (AO) of Si. In the other minimum **9**, which is 4.4 kcal mol^{-1} higher in energy, the hydrogens are nearly anti ($\omega = 150°$) with respect to the SOMO.



8



9

In order to interpret the absorption spectrum of the $(MeS)_3Si^{\bullet}$ radical, MSX_{α} calculations were performed on this radical at the geometry obtained by replacing hydrogens with methyl groups and assuming standard bond lengths and standard bond angles for the methyl group.

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The results are reported in Table III. On the basis of the energies and oscillator strengths of the vertical transitions, the weak band at ca. 425 nm could be attributed to the valence excitation from the MO localized at the Si–S bond to the SOMO localized mainly at the 3p AO of Si. The distribution in the SOMO is 71% on silicon (24% in 3s, 74% in 3p, and 2% in 3d) and 24% on sulfur atoms (87% p and 13% d). In accord with experiment, the corresponding transition from the MO localized at the Si–C bond in the trimethylsilyl radical[33] was computed at a much lower wavelength (316 nm), in the range of the 4p Rydberg transitions. This result indicates that the σ_{Si-C} MO lies at lower energy with respect to the σ_{Si-S} MO. The strong band at 300–310 nm could be attributed to transitions from the SOMO to the antibonding σ^*_{Si-S} MOs (a_1 and e symmetry). Contributions to intensity of this band could also be derived from the valence transition from the σ_{Si-S} MO to the SOMO and from the transition to 4p Rydberg orbital, which was computed to occur in this region in the trimethylsilyl radical. However, it should be remarked that at variance with the trimethylsilyl radical a sizeable mixing occurs between Rydberg and valence excited states in the $(MeS)_3Si^\bullet$ radical. Transitions from sulfur lone pairs to the SOMO have much lower oscillator strengths and are predicted to occur in the near infrared region as in perthiyl radicals.[34]

Photoacoustic Calorimetry. In laser-induced photoacoustic calorimetry the combined heats of reactions 8 and 9, $\Delta H_8 + 2\Delta H_9$ (or $\Delta H_{8,9}$), is determined by measuring the net heat deposition in solution. The net enthalpy change associated with reactions 8 and 9 is given by eq 11,

$$\Delta H_{8,9} = 84.8(1 - a_R/a_C)/\Phi \qquad (11)$$

where the energy provided by the photon (337.1 nm) is 84.8 kcal mol^{-1}, Φ is the quantum yield for photolysis of the di-*tert*-butyl peroxide in benzene (0.85), and a_R and a_C are the slopes obtained from the plots of photoacoustic signal amplitude, N, versus the amount of light absorbed by the photoreactive species $(1 - T)$ for the silane and calibration runs, respectively.[35] The experimental results from eq 11 are used along with the thermodynamic relationships of eqs 12 and 13 to derive the Si–H bond dissociation enthalpy, DH°[(RS)$_3$Si–H]. That is, combination of these results with the literature values for the heats of formation of Me_3COH,[36] $Me_3COOCMe_3$,[37] and $H^\bullet$ [36] led to the bond dissociation enthalpy in the silanes (eq 14), where the heats of formation of the precursor silane and the silyl radicals do not factor into the final result.

$$\Delta H_{8,9} = 2\Delta H_f(Me_3COH) + 2\Delta H_f[(RS)_3Si^\bullet] + \Delta H_f(Me_3COOCMe_3) + 2\Delta H_f[(RS)_3SiH] \qquad (12)$$

$$DH^\circ[(RS)_3Si{-}H] = \Delta H_f[(RS)_3Si^\bullet] + \Delta H_f(H^\bullet) + \Delta H_f[(RS)_3SiH] \qquad (13)$$

$$DH^\circ[(RS)_3Si{-}H] = \Delta H_{8,9}/2 + 86.1 \text{ kcal mol}^{-1} \qquad (14)$$

It has previously been reported that the photoacoustic experiment is subject to time constaints introduced by the transducers.[38] Since the responses of the transducers used in this work were 0.5 MHz (2.2 μs), then the heat evolved from reactions 8 and 9 must be released within a period of time that is much shorter than this. The concentrations of **1** and **2** were adjusted so that the reactions were complete within ca. 60 ns (0.3–0.6 M). In addition, the laser output was attenuated by the use of an iris and neutral density filters so that contributions from second-order processes (specifically radical–radical reactions) did not contribute to the net heat evolved during the response of the transducers.

Two determinations each were made for the bond dissociation enthalpy for silanes **1** and **2** in benzene at 22 °C. In the case of **1**, the average of the two determinations gave DH°[(MeS)$_3$Si–H] = 82.5 ± 0.7 kcal mol^{-1}. However, experiments on the more heavily substituted compound **2** gave bond dissociation enthalpies about 3 kcal mol^{-1} higher. As revealed by the kinetic experiments performed on $(MeS)_3SiH$ and $(MeS)_4Si$ and also $(i\text{-}PrS)_3SiH$ and $(i\text{-}PrS)_4Si$, we were able to determine that >99% of the *tert*-butoxyl radicals abstract hydrogen from the Si–H moiety. We therefore feel confident that contributions to DH°(Si–H) by reaction 15 are completely neglible. The

$$Me_3CO^\bullet + (RS)_3SiH \rightarrow Me_3COH + [R(-H)S]_3SiH \qquad (15)$$

results are summarized in Table II along with values previously determined for Et_3SiH an $(Me_3Si)_3SiH$. Sulfur substitution next to silicon introduces a substantial heteroatom effect as DH°(Si–H) in tris(methylthio)silane is 7–8 kcal mol^{-1} lower than that for Et_3SiH, but ca. 4 kcal mol^{-1} higher than that for the Si–H bond in $(Me_3Si)_3SiH$. Interestingly, preliminary results for a number of siloxanes show that oxygen contributes virtually no heteroatom effect on the Si–H bond dissociation enthalpy in these compounds.[39] DH°(Si–H) appears to vary insignificantly from that for trialkylsilanes such as Et_3SiH. This lends support for the argument that the silyl radicals formed from $(RS)_3SiH$ and $(Me_3Si)_3SiH$ are stabilized by interactions such as (d–3p)π type bonding or/and hyperconjugation.

Conclusions

Tris(alkylthio)silanes function as free radical reducing agents for a variety of organic substrates as well as hydrosilylating agents for alkenes having electron-donating substituents. The main features of these silanes are that (i) their Si–H bond dissociation energies are close to those Ge–H in trialkylgermanium hydrides, which makes them attractive alternatives from the hydrogen-donor point of view,[40] and (ii) the corresponding silyl radicals are found to be more electrophilic than other organometallic group 14-centered radicals and, consequently, a different chemoselectivity is expected in reduction reactions with respect to the majority of other radical-based reducing agents.[40] Further work on the kinetics and synthetic scope of these reactions is in progress.

Experimental Section

Materials. Tris(alkylthio)silanes,[16] cyclohexyl selenide,[41] and cyclohexyl xanthate[42] were prepared following literature procedures. Tetrakis(alkylthio)silanes was obtained from tris(alkyl-

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thio)silyl chloride and the corresponding sodium alkanethiolate. All other materials were commercially available and used as received. 2-Hydroxybenzophenone was recrystallized twice from ethanol. Di-*tert*-butyl peroxide was passed through neutral alumina at least three times before use.

Tetrakis(methylthio)silane: mp 32–33 °C; ^{1}H NMR (200 MHz, C_6D_6) δ 1.90 (s, 12 H); ^{13}C NMR (50.3 MHz, C_6D_6) δ 9.9; GC/MS *m/e* 216 (M^+), 169. Anal. Calcd for $C_4H_{12}S_4Si$: C, 22.23; H, 5.60. Found: C, 21.40; H, 5.52.

Tetrakis(isopropylthio)silane: mp 38–40 °C; bp 120 °C (0.05 mbar); ^{1}H NMR (200 MHz, C_6D_6) δ 3.62 (m, 4 H, J = 6.8 Hz), 1.32 (d, 24 H, J = 6.8 Hz); ^{13}C NMR (50.3 MHz, C_6D_6) δ 36.5, 27.1; GC/MS *m/e* 328 (M^+), 285, 253, 127. Anal. Calcd for $C_{12}H_{28}S_4Si$: C, 43.89; H, 8.60. Found: C, 43.55; H, 8.58.

General Procedure for Reduction of Organic Derivatives (Table I). A solution containing the compound to be reduced, tris(alkylthio)silane (1.2 equiv), and AIBN (ca. 10%) as initiator in toluene was heated at 75–90 °C for 0.5–2.5 h and then analyzed by GC. Yields were quantified by GC using dodecane or tetradecane as an internal standard.

General Procedure for Hydrosilylation of Alkenes. A 20-mL two-necked round-bottoned flask equipped with a magnetic stirring bar, dry argon inlet, reflux condenser, and septum was charged with 1 mmol of alkene, 1.2 mmol of $(MeS)_3SiH$, and 0.15 mmol of AIBN in 10 mL of toluene. The solution was heated at 85 °C for 2–3 h until the alkene was consumed (followed by GC). The reaction mixture was concentrated in vacuo. Distilation gave 83–89% of product.

1-[Tris(methylthio)silyl]decane: bp 90 °C (0.05 mbar); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.11 (s, 9 H), 1.11–1.53 (m, 18 H), 0.88 (t, 3 H, J = 6.4 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 9.3 (3 Me), 13.8 (Me), 17.5 ($SiCH_2$), 22.4, 23.1, 28.9, 29.1, 29.3, 29.4, 31.7, 32.5 ($8CH_2$). Anal. Calcd for $C_{13}H_{30}S_3Si$: C, 50.26; H, 9.73. Found: C, 50.30; H, 9.71.

2-[Tris(methylthio)silyl]ethyl butyl ether: bp 120 °C (0.05 mbar); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.61 (m, 2 H), 3.41 (t, 2 H, J = 6.6 Hz), 2.11 (s, 9 H), 1.32–1.58 (m, 6 H), 0.91 (t, 3 H, J = 7.3 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 9.3 (3 Me), 13.6 (Me), 19.1, 19.4, 31.6, 65.9, 70.4 (5 CH_2); GC/MS *m/e* 197 (M^+ − OBu), 169, 138. Anal. Calcd for $C_9H_{22}S_3Si$: C, 42.47; H, 8.71. Found: C, 42.25; H, 8.66.

7-[Tris(methylthio)silyl]-Δ^1-*p*-menthene: bp 120 °C (0.05 mbar); ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.38 (m, 1 H), 2.12 (s, 9 H), 1.13–2.04 (m, 10 H), 0.88 (dd, 6 H, J = 6.7, 2.5 Hz); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 131.3, 122.9, 39.7, 32.2, 31.6, 29.3, 28.5, 26.6, 19.9, 19.7, 0.93; GC/MS *m/e* 306 (M^+), 258, 170, 168, 122. Anal. Calcd for $C_{13}H_{26}S_3Si$: C, 50.92; H, 8.55. Found: C, 51.15; H, 8.61.

Laser Flash Photolysis. The technique of laser flash photolysis was used to determine the kinetics of hydrogen abstraction and to characterize the radical absorption spectra. Experiments were carried out using the pulses from a Molectron UV-24 nitrogen laser (337.1 nm, ~8 ns, ~10 mJ/pulse). The complete apparatus and experimental technique have been described elsewhere.[43] All experiments were carried out on deaerated samples under nitrogen atmospheres.

Photoacoustic Calorimeter. The photoacoustic calorimeter used in this work has been described in detail elsewhere.[44] Briefly, pulses from a Molectron UV-24 nitrogen laser (337.1 nm, ~8 ns, ~10 mJ/pulse, 2–3 Hz) were used to irradiate argon-purged solutions contained in standard 6.6 × 10-mm (internal dimensions) quartz luminescence flow cells (Helma 174). Photolysis of the solutions gave rise to shock waves that were detected by a piezoelectric transducer (Panametrics V101, 0.5 MHz) in contact with the bottom of the cuvette. The transducer signals were amplified (Panametric ultrasonic preamplifiers) and the analog signals were relayed to a programmable digitizer/oscilloscope (Tetroniks 7D20/7603). A beam-splitter was placed in front of the sample cuvette to account for the variation in laser beam intensity; a fraction of the laser beam was directed at a reference cuvette/transducer/amplifier arrangement, as described above, containing ca. 10^{-4} M 2-hydroxybenzophenone in benzene. Since it is well known that 2-hydroxybenzophenone converts 100% of excitation energy to heat,[45] the signal from the reference cuvette served to normalize the signal from the sample cuvette correcting for any variation in laser beam intensity. The total heat evolved by reactions 9 and 10, $\Delta H_{9,10}$, was determined by varying the concentration of di-*tert*-butyl peroxide over a range of 2–12% v/v at a fixed silane concentration and laser output. The slope a_R, from a plot of the normalized photoacoustic signal amplitude versus the fraction of light absorbed by di-*tert*-butyl peroxide, $1 - T$ (or $1 - 10^{-OD}$), is directly proportional to the enthalpy balance of reactions 8 and 9. Typically 3–4 runs of 258 laser shots were averaged to produce a data point for analysis.

Since photoacoustic calorimetry is a comparative technique, the apparatus required calibration before each experiment. 2-Hydroxybenzophenone, which dissipates 100% of its excitation energy in the form of heat was used as a calibrant in this experiment (and also as an energy monitor as described above). The apparatus was calibrated following the procedure described above for the reaction of di-*tert*-butyl peroxide with the substrate silane (no di-*tert*-butyl peroxide was present in the calibration runs) providing a calibration constant, a_C.[46]

Computational Details. Multiple scattering X_α (MSX_α) calculations were performed on the $(CH_3S)_3Si^\bullet$ radical in order to assign the features in the optical absorption spectrum. A C_{3v} symmetry was assumed with the CH_3 group eclipsing the singly occupied molecular orbital (SOMO) on the silane atom. Some structural parameters have been taken from the optimum geometry of the parent $(HS)_3Si^\bullet$ radical obtained with ab initio calculations at the 6-31G* level of theory utilizing the GAUSSIAN86 system of programs,[47] i.e., r_{Si-S} = 2.1485 Å, SSiS = 108.99°, SiSC = 92.17°. Since the optimaized r_{S-H} = 1.329 Å is close to its standard value (1.332 Å),[48] standard S–C bond lengths (r_{S-C} = 1.817 A) were utilized in the $(CH_3S)_3Si^\bullet$ radical. Standard bond lengths (r_{C-H} = 1.096 Å) and bond angles (HCH = 109.47°) have also been used for methyl group.

The computation procedure MSX_α-DC described in ref 33 has been employed to compute the transition energies and oscillator strengths. This procedure has been shown to provide a reliable estimate of the excitation energies in radicals. Particularly, in $R_3M^\bullet$ radicals having such a high symmetry (C_{3v}) as that assumed for the $(CH_3S)_3Si^\bullet$ radical, vertical transition energies both to Rydberg and valence orbitals were reproduced with great accuracy, the deviation from experiments being about 2000 cm^{-1}. This accuracy is compared to that obtained with CI calculations employing large basis sets. Wave functions were expanded in partial waves up to $l = 1$ (sp) in the hydrogen, $l = 2$ (spd) in the carbon, $l = 3$ (spdf) in the silicon and sulfur, and $l = 4$ (spdfg) in the outer spheres. The outsphere center was located at the barycenter of the valence electrons.

Acknowledgment. This work was supported by the Progetto Finalizzato Chimica Fine II (CNR-Rome).

Registry No. **1**, 18230-81-4; **2**, 17891-55-3; **3**, 2695-47-8; **4**, 592-41-6; **5**, 96-37-7; **6**, 110-82-7; **7** (X = MeS), 139461-44-2; **7** (X = *i*-PrS), 139461-45-3; $CH_3(CH_2)_{14}CH_3$, 544-76-3; $PhCOCH_3$, 98-86-2; Me_3SiCH_3, 75-76-3; $Me_3COC(O)CH_3$, 540-88-5; $(MeS)_3Si(CH_2)_9CH_3$, 139493-24-6; $(MeS)_3Si(CH_2)_2O(CH_2)_3CH_3$, 139493-25-7; $CH_3(CH_2)_{14}CH_2Br$, 112-82-3; $PhCOCH_2Br$, 70-11-1; $CH_3(CH_2)_{14}CH_2I$, 544-77-4; Me_3SiCH_2NC, 30718-17-3; $Me_3COC(O)CH_2NC$, 2769-72-4; $CH_2{=}CH(CH_2)_7CH_3$, 872-05-9; $CH_2{=}CHO(CH_2)_3CH_3$, 111-34-2; $(Me_3Si)_3SiH$, 1873-77-4; $(MeS)_3Si^\bullet$,

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Interaction of an Allene with Polyvalent Iodine Derivatives. Preparation, X-ray Molecular Structure, and Some Reactions of Phenyl(2,2-dimethyl-4-(diethylphosphono)-2,5-dihydro-3-furyl)iodonium Salts

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Received November 22, 1991

Allene **1** reacts with PhIO/BF$_3$·Et$_2$O or PhIF$_2$/BF$_3$·Et$_2$O in CH$_2$Cl$_2$ at −60 °C with the formation of novel phenyldihydrofuryliodonium salts **2**. Molecular structures for both products **2a,b** are determined by X-ray analysis. Iodonium perchlorate **2b** reacts with the anionic nucleophiles (NaN$_3$, NaOCH$_3$, NaOC$_2$H$_5$, CuI/KI) to give the corresponding products of the vinylic nucleophilic substitution (**6a–e**) of the iodobenzene moiety. However, analogous reaction of **2b** with Ph$_3$P gives an unexpected iodide **6e** as the major product, along with the usual product of nucleophilic substitution (**6d**). This result is rationalized by a nucleophilic attack of Ph$_3$P on the iodine atom of the iodonium salt **2b** followed by two alternative paths for subsequent ligand coupling.

Introduction

There is widespread current interest in iodonium chemistry.[1] Considerable effort has been devoted to the search for new methods of synthesis, structure investigation, and synthetic application for alkynyl,[2] vinyl,[2c,3,4] and allenylphenyliodonium[2i,5] salts. To date the great majority of the preparations of iodonium salts containing unsaturated moieties are based on the transformation of vinyl and acetylenic derivatives by the action of polyvalent iodine reagents.[2-5] To our knowledge there is only a single example of the reaction of a trivalent iodine reagent, namely [hydroxy(tosyloxy)iodo]benzene, with allenes which, however, proceeds to give ketones and not unsaturated iodonium derivatives.[6] Such reactions may lead to the synthesis of valuable new vinyliodonium compounds and, in the case of substituted allenes, to the question of the regio- and stereoselectivity of these reactions as well as the possible participation of nucleophilic substituents in the final step of addition.

The high leaving-group ability of the phenyliodonio moiety causes instability of vinylphenyliodonium salts under acidic, basic, and neutral conditions.[3a-f] Some of them undergo very facile β-elimination yielding the corresponding terminal alkynes.[3a-c,f] Reactions of these salts with nucleophiles allow vinylic nucleophilic substitution with partial or complete inversion of configuration.[3c,f] A

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