mixture was purified by HPLC (EtOAc/hexane, 1:1) to give 13 (28%) as pale yellow crystals: mp 131–132 °C dec; ^{1}H NMR (200 MHz) δ 4.00–4.12 (2 H, m), 5.67–5.70 (1 H, m), 7.11–7.15 (1 H, m), 7.53–7.88 (3 H, m), 8.02–8.08 (2 H, m); IR (KBr) 2231, 1678, 1327, 1282, 1145 cm^{-1}; MS *m/z* 247 (M$^+$), 183, 105 (100), 77; HRMS calcd for $C_{12}H_9NO_3S$ 247.0303, found 247.0306. The purity of 13 was judged to be ≥90% by ^{1}H NMR spectral determinations.

3-(Methoxycarbonyl)-2,2-dimethyl-2,5-dihydrothiophene 1,1-Dioxide (14). To a stirred solution of **9a** (0.2701 g, 1.42 mmol) in THF (30 mL) was added *n*-BuLi (1.68 mL, 1.69 M, 2.84 mmol) in cyclohexane dropwise at −105 °C, and the temperature was raised gradually to −90 °C. CH_3I (0.18 ml, 2.84 mmol) was added, and the reaction was slowly warmed to −78 °C. The reaction was quenched with saturated NH_4Cl, extracted into EtOAc, dried ($MgSO_4$), and concentrated. The yellow oil was purified with a silica gel column (EtOAc/hexane, 1:2) to give 14 (0.2685 g, 92%) as white crystals: mp 77–78 °C dec: ^{1}H NMR (200 MHz) δ 1.61 (6 H, s), 3.82 (3 H, s), 3.86 (2 H, d, $J = 3.3$ Hz), 7.00 (1 H, t, $J = 3.3$ Hz); IR (KBr) 1708, 1431, 1329, 1291, 1161, 1115 cm^{-1}; MS *m/z* 173 (M$^+$ − 31), 140 (100), 108. Anal. Calcd for $C_8H_{12}O_4S$: C, 47.04; H, 5.92. Found: C, 47.06; H, 6.15.

Acknowledgment. We thank the National Science Council of the Republic of China for financial supports.

Registry No. **1a**, 67488-50-0; **1b**, 108919-91-1; **1c**, 122131-77-5; **2a**, 104664-92-8; **2b**, 127844-17-1; **2c**, 128114-75-0; **3c**, 128114-76-1; **4**, 128114-77-2; **5**, 128114-78-3; **6**, 128114-79-4; **9a**, 128114-80-7; **9b**, 123559-84-2; **9c**, 128114-81-8; **10**, 128114-82-9; **11**, 128114-83-0; **12**, 128114-84-1; **13**, 128114-85-2; **14**, 128114-86-3; 2-methyl-3-(phenylsulfonyl)-2,3-dihydrothiophene 1,1-dioxide, 123559-85-3.

Supplementary Material Available: ^{1}H NMR spectra for compounds **2c**, **3c**, and **13** (3 pages). Ordering information is given on any current masthead page.

Triphenylsilane: A Useful Radical-Based Reducing Agent[1]

M. Lesage,[1] J. A. Martinho Simões,[*,2] and D. Griller[*,1]

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6, and Centro de Quimica Estrutural, Instituto Superior Têcnico, 1096 Lisbon Codex, Portugal

Received November 3, 1989

It has been shown that tris(trimethylsilyl)silane is effective in reducing organic halides by a free-radical mechanism whereas simple trialkylsilanes are far less efficient.[3,4] This discovery followed from measurements of silicon–hydrogen bond dissociation enthalpies[5] since D{$(Me_3Si)_3Si$–H} = 79 kcal mol^{-1} as opposed to D(Et_3Si–H) = 91 kcal mol^{-1}. This implies that the crucial chain carrying step in the reduction, i.e. hydrogen abstraction by simple alkyl radicals from tris(trimethylsilyl)silane, is exothermic by roughly 19 kcal mol^{-1} whereas for trialkylsilanes the corresponding figure is only about 7 kcal mol^{-1}.

In the course of our investigations on the effects of other substituents on D(Si–H), we have found that phenyl groups also induce a weakening of the silicon–hydrogen bond.[6] Although the effect is not as dramatic as for the silyl moieties, D(Si–H) in triphenylsilane is about 7 kcal mol^{-1} lower than D(Et_3Si–H),[6,7] suggesting that Ph_3SiH would also be a useful reducing agent at moderate temperatures. Results for the kinetics of reduction of bromohexadecane by several phenyl-substituted silanes are now reported and confirm that suggestion.

Experimental Section

Triphenylsilane, diphenylmethylsilane, phenyldimethylsilane, and the remaining materials used in the experiments were commercially available.

In a typical experiment, 11 mg of dibenzoyl peroxide (0.0087 M) were added to 5 mL of a heptane solution of Ph_3SiH (0.067 M), bromohexadecane (0.052 M), and undecane (internal standard; 100 μL). The mixture was kept at 90 ± 2 °C, and the reaction was followed quantitatively by gas chromatography (Hewlett-Packard 5890) over a period of about 5 h and to >80% conversion of the bromide. Products were identified by GC/mass spectrometry (Hewlett-Packard 5970A). Both instruments were equipped with cross-linked methylsilicon columns, and authentic samples of reagents and products were used for calibration. The same procedure was used in the competition experiments involving Ph_3SiH and the other silanes. However, the low reactivity of Ph_2MeSiH and $PhMe_2SiH$ required an increase of dibenzoyl peroxide concentration to ca. 0.025 M in the case of Ph_2MeSiH and 0.03 M for $PhMe_2SiH$. The relative concentrations of each pair of silanes were adjusted so as to optimize the experimental conditions, e.g. [Ph_3SiH]:[Ph_2MeSiH] = 1:3 and [Ph_3SiH]:[$PhMe_2SiH$] = 1:4.

Results and Discussion

A kinetic description of the radical chain mechanism reactions 1–5 was formulated by applying the steady-state approximation to [R$'^\bullet$] and by assuming that the consumption of silane in reaction 2 was negligible. Since halogen abstraction by silyl radicals is extremely rapid,[8,9] reaction 4 must represent the rate determining propagation step. The result is given in eq 6. Plots of ln ([R_3SiH]/[R_3SiH]$_0$) versus $e^{-k_1t/2}$ (Figure 1) led to values for $2k_4{}^2/k_1k_5$. For triphenylsilane (R = Ph), we found $k_4 = (3.0 \pm 0.3) \times 10^4\ M^{-1}\ s^{-1}$ at 90 °C in heptane by applying literature data[10,11] for k_1 ($5.9 \times 10^{-5}\ s^{-1}$) and k_5 ($1.3 \times 10^{10}\ M^{-1}\ s^{-1}$).

$$(PhCO)_2 \xrightarrow{k_1} PhCO_2^\bullet \rightarrow Ph^\bullet + CO_2 \qquad (1)$$

$$PhCO_2^\bullet/Ph^\bullet + R_3SiH \xrightarrow{k_2} R_3Si^\bullet + PhCO_2H/PhH \qquad (2)$$

$$R_3Si^\bullet + R'Br \xrightarrow{k_3} R'^\bullet + R_3SiBr \qquad (3)$$

$$R'^\bullet + R_3SiH \xrightarrow{k_4} R_3Si^\bullet + R'H \qquad (4)$$

$$R'^\bullet + R'^\bullet \xrightarrow{k_5} R'R \qquad (5)$$

$$\ln([R_3SiH]_o/[R_3SiH]_0) = \{2k_4{}^2[(PhCO_2)_2]_0/k_1k_5\}(e^{-k_1t/2} - 1) \qquad (6)$$

The error quoted for k_4 does not include uncertainties associated with k_1 and k_5. However, its order of magnitude confirms the thermochemically based suggestion that Ph_3SiH is a useful reducing agent.[12] Moreover, the value

---

(1) National Research Council, Issued as NRCC publication No. 31398.

(2) Centro de Quimica Estrutural.

(3) Chatgilialoglu, C.; Griller, D.; Lesage, M. *J. Org. Chem.* **1988**, *53*, 3641.

(4) Lesage, M.; Chatgilialoglu, C.; Griller, D. *Tetrahedron Lett.* **1989**, *30*, 2733.

(5) Kanabus-Kaminska, J. M.; Hawari, J. A.; Griller, D.; Chatgilialoglu, C. *J. Am. Chem. Soc.* **1987**, *109*, 5267.

(6) Griller, D.; Kanabus-Kaminska, J. M.; Martinho Simões, J. A., submitted for publication.

(7) Walsh, R. In *The Chemistry of Organo Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1988.

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

(9) Chatgilialoglu, C.; Griller, D.; Lesage, M. *J. Org. Chem.* **1989**, *54*, 2492.

(10) Calculated by taking data for the self-reaction of the benzyl radical in toluene and by correcting for differences in temperature and solvent viscosity. Griller, D. In *Landolt Börnstein*; Fischer, H., Ed.; Springer Verlag: New York, 1984; New Series, Group II, Vol. 13a, Part 1, p 5. Schuh, H.-H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2130.

(11) (a) Walling, C. *Tetrahedron* **1985**, *41*, 3887. (b) Koenig, T. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol I. (c) Smid, J.; Rembaum, A.; Szwarc, M. *J. Am. Chem. Soc.* **1956**, *78*, 3315. (d) Nozaki, K.; Bartlett, P. D. *J. Am. Chem. Soc.* **1946**, *68*, 1686.

0022-3263/90/1955-5413$02.50/0 Published 1990 by the American Chemical Society

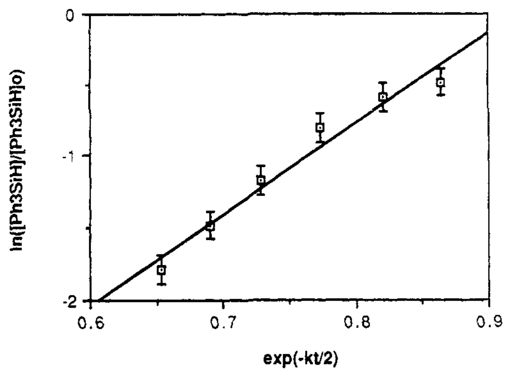

Figure 1. Plot of ln ($[Ph_3SiH]/[Ph_3SiH]_0$) versus $e^{-k_1t/2}$ for the benzoyl peroxide initiated reduction of bromohexadecane in heptane solvent at 90 °C.

found for k_4 is close to the average of values (2×10^4 M^{-1} s^{-1} at 50 °C in benzene) reported by Newcomb and Park[13] who used a competition technique to estimate the rate constant.

From a practical perspective, the GC results indicated that 50% of bromohexadecane was reduced after 1.4 h and that the yield of the reaction was over 80% after 4 h. The chain length at the start of the experiment was 18, which is respectable for applications in synthesis.

The competition experiments involving Ph_2MeSiH or $PhMe_2SiH$ led to more reliable results since the ratio of the rate constants k_4/k'_4, eq 7, did not depend on data for k_1 and k_5. The values obtained, 1.60 ± 0.03 and 2.63 ± 0.14 for R_3SiH = Ph_2MeSiH and $PhMe_2SiH$, respectively, show a noticeable decrease of the reaction rate when the number of phenyl groups bonded to the silicon atom decreases. The values obtained in the competition experiments can be combined with that for k_4 to give $k'_4 = (1.9 \pm 0.25) \times 10^4$ M^{-1} s^{-1} (Ph_2MeSiH) and $(1.1 \pm 0.15) \times 10^4$ M^{-1} s^{-1} ($PhMe_2SiH$). For R_3SiH = Et_3SiH, no significant reduction of bromohexadecane was observed under the same experimental conditions. The results indicate that Ph_2MeSiH and $PhMe_2SiH$ are probably impractical agents because reaction chain lengths would be unacceptably small.

$$\frac{\ln ([Ph_3SiH]/[Ph_3SiH]_0)}{\ln ([R_3SiH]/[R_3SiH]_0)} = \frac{k_4}{k'_4} \qquad (7)$$

In radical-based reductions of alkyl halides, rapidity of hydrogen transfer is not necessarily a virtue. If the synthesis requires that a radical rearrangement takes place before the transfer step, then slowness may be a desirable characteristic given the limitation that the reactions must proceed with reasonable chain length to give decent yields. It has been suggested[14,15] that tributylgermane is a suitable reagent for this purpose, although its high cost tends to make this application unattractive. The above results suggest that triphenylsilane may be a good alternative when primary alkyl radicals are involved in hydrogen abstraction at the Si–H bond.

Registry No. Ph_3SiH, 789-25-3; Ph_2MeSiH, 776-76-1; $PhMe_2SiH$, 766-77-8; bromohexadecane, 112-82-3.

---

(12) See, for example: (a) Nagai, Y.; Yamazaki, K.; Shiojima, I. *J. Organomet. Chem.* **1967**, *9*, 21. (b) Nagai, Y.; Matsumoto, H.; Hayashi, M.; Tajima, E.; Watanabe, H. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3113. (c) Sakurai, H.; Yamagota, M.; Murakami, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2658. (d) Sommer, L. H.; Ulland, L. A. *J. Am. Chem. Soc.* **1972**, *94*, 3803.

(13) Newcomb, M.; Park, S. U. *J. Am. Chem. Soc.* **1986**, *108*, 4132.

(14) Lusztyk, J.; Maillard, B.; Deycard, S.; Lindsay, D. A.; Ingold, K. U. *J. Org. Chem.* **1987**, *52*, 3509.

(15) Lusztyk, J.; Maillard, B.; Lindsay, D. A.; Ingold, K. U. *J. Am. Chem. Soc.* **1983**, *105*, 3578.

Exploratory Studies of the Photochemistry of *N*-Hydroxypyridine-2-thione Esters. Generation of Excited Radicals by Laser Flash Photolysis and in a Conventional Fluorescence Spectrometer[1]

C. Bohne,[2] R. Boch,[3] and J. C. Scaiano*[2,3]

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6, and Department of Chemistry, University of Ottawa, Ottawa, Canada K1N 6N5

Received March 16, 1990

Introduction

Since their introduction by Barton et al., chain reactions of *N*-hydroxypyridine-2-thione esters have been extensively used for synthetic purposes.[4,5] The reaction (Scheme I) is initiated by addition of a radical, generated thermally or photochemically, to the thione's sulfur center. Normally, the $RCO_2^\bullet$ radical decarboxylates rapidly leading to $R^\bullet$, which either propagates the chain by adding to the thione, or undergoes other reactions (e.g. rearrangements, hydrogen abstraction, etc.), ultimately leading to a chain carrier radical.

Competitive studies have led to rate constants of 2×10^6 (50 °C) and 4.6×10^5 M^{-1} s^{-1} (30 °C) for the addition of primary and tertiary carbon radicals to their precursor, respectively.[6,7] The kinetics with which carbon-centered radicals react with their precursors are important when *N*-hydroxypyridine-2-thione esters are used for synthetic purposes, since this reaction will determine whether the chain carrier will give the desired product or not.

Little is known about the primary photochemistry of *N*-hydroxypyridine-2-thione esters, although it has been established that extensive cleavage of the N–O bond takes place. The esters are excellent precursors for free radicals for EPR work,[8] but an earlier attempt to monitor the radicals by laser flash photolysis was unsuccessful as a result of interference by the strong UV–visible absorption of the starting esters.[8]

This study was undertaken in an attempt to learn some of the details of the primary photochemistry of these compounds. The compounds in Scheme II were selected for study, since upon N–O cleavage they are expected to yield radicals with very different kinetic and spectroscopic characteristics. For the diphenylacetic acid derivative (I) we expect rapid decarboxylation of $Ph_2CHCO_2^\bullet$ to yield the readily detectable diphenylmethyl radical,[9] with a very strong absorption band at 330 nm. Cleavage of the *p*-methoxybenzoic acid derivative (II) should lead to *p*-$CH_3OC_6H_4CO_2^\bullet$ radicals with a characteristic absorption band at $\lambda > 600$ nm and lifetimes of several microseconds in solvents such as carbon tetrachloride, acetonitrile, and Freon-113.[10] Finally, the 2,2-dimethylvaleric acid derivative (III) was used as a control in laser experiments, since the 2-methyl-2-pentyl radical is not expected to show

---

(1) Issued as NRCC-31523.

(2) NRCC.

(3) University of Ottawa.

(4) Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron* **1985**, *41*, 3901.

(5) Barton, D. H. R.; Zard, S. Z. *Pure Appl. Chem.* **1986**, *58*, 675.

(6) Newcomb, M.; Park, S. U. *J. Am. Chem. Soc.* **1986**, *108*, 4132.

(7) Newcomb, M.; Kaplan, J. *Tetrahedron Lett.* **1987**, *28*, 1615.

(8) Ingold, K. U.; Lusztyk, J.; Maillard, B.; Walton, J. C. *Tetrahedron Lett.* **1988**, *29*, 917.

(9) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.

(10) Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* 1988, *110*, 2877.

0022-3263/90/1955-5414$02.50/0