

0040-4039(95)00593-5

## 5,10-Dihydro-Silanthrene as a Reagent for the Barton-McCombie Reaction

T. Gimisis, M. Ballestri, C. Ferreri,<sup>1</sup> and C. Chatgilialoglu\*

I.Co.C.E.A., Consiglio Nazionale delle Ricerche, Via P. Gobetti 101, 40129 Bologna, Italy

## R. Boukherroub and G. Manuel

Laboratoire d'Hétérochimie Fondamentale et Appliquée, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse, France

Abstract: The deoxygenation of secondary alcohols via thionoesters with the use of 5,10-dihydrosilanthrene as the radical reducing agent has been studied in detail. The ability of hydrogen donation of this silane has been measured using the one-carbon ring expansion of 1-(2-oxocyclopentyl)ethyl radical as a timing device.

The Barton-McCombie reaction, first reported 20 years ago,<sup>2</sup> has been established as the method of choice for the deoxygenation of secondary alcohols in organic synthesis (eq. 1). Although tin hydrides were initially used as hydrogen donors in this mild free radical process,<sup>3</sup> there have been research efforts, especially during the last five years, to replace the fetid, toxic, and chromatographically incommodious tri-*n*-butyltin hydride with other sources of hydrogen radical donors.<sup>4</sup>

$$ROH \longrightarrow R-O-C-Z \xrightarrow{Bu_3SnH} RH$$
(1)

Tris(trimethylsilyl)silane has proven a valuable alternative to tin hydrides also in the Barton-McCombie reaction.<sup>4,5</sup> Other silanes such as triethyl<sup>6</sup>, phenyl<sup>7</sup>, diphenyl<sup>8</sup> and triphenylsilane<sup>9</sup> have been used for the radical deoxygenation of alcohols but in these cases more drastic conditions are required due to the lower hydrogen donation abilities of these hydrides relative to (TMS)<sub>3</sub>SiH.<sup>4,10</sup> The higher bond strengths result in shorter radical chains that become synthetically useful only at higher temperatures (125-140 °C), with a large excess of reagents and/or stoichiometric amounts of initiators.

5,10-Dihydro-silanthrenes 1a and 1b were recently introduced by Oba and Nishiyama<sup>11</sup> as radical reducing agents and were successfully applied to the Barton-McCombie methodology. Continuing our



work directed towards the discovery of efficient hydrogen radical donors,<sup>4,5</sup> we had been working on the unsubstituted analogue  $(2)^{12}$  when this communication appeared, and we now wish to report our results related to the reductive ability of 5,10-dihydro-silanthrene (2).

In order to test the reducing abilities of silane 2, a variety of thiono esters of cyclododecyl alcohol, i.e. compounds 3a-3d,<sup>13</sup> were prepared. An *n*-nonane solution containing a thiono ester derivative 3 (0.2 M), 1.5 equiv. of silane 2 and AIBN(10%) as a radical initiator was heated for 2h at 80°C (the standard experimental conditions also used for (TMS)<sub>3</sub>SiH and Bu<sub>3</sub>SnH) and was consequently analysed by GC. Yields were quantified by using an internal standard (n-undecane) and are reported in Table 1. Phenyl thionocarbonate 3a gave an excellent yield, but surprisingly, incomplete conversions and lower yields were observed with the corresponding xanthate, thiocarbonyl imidazolide and N-phenyl thioxocarbamate. The reduction of 3a in either aromatic solvents or at room temperature using triethylborane/O<sub>2</sub> as the radical initiator is still an efficient process. In all other cases, improved yields were observed by running the reaction in toluene (Table 1). However, all subsequent attempts to optimize the experimental conditions (e.g., higher temperatures, stoichiometric amounts of initiator, excess hydride) did not provide any significant amelioration. These results could suggest that with substrates other than phenyl thionocarbonates there is a build-up of an inhibitory species as the reaction progresses. This hypothesis was further corroborated by competition experiments which showed that phenyl thionocarbonate 3a is not converted completely to the corresponding deoxygenated product 3e, in the presence of 3b or 3c. The nature of the postulated inhibitor [currently believed to be of the general structure ZC(O)SH] and the mechanism of its formation is currently under investigation.

Table	1.	Reduction	01	some	organic	derivatives	bу	snane	2ª	
		<b>~~</b>								-

Deduction of come expension destructions 1 with a 22

product	yield, <sup>b,c</sup> %	Substrate	product	yield, <sup>d</sup> %
3e	99 (96)	4a	4b	91
3e	65 (70)	5a	5 b	85
3e	20 (46)	6a	6 b	96
3e	23 (32)			
Į	3e 3e 3e 3e 3e	product         yield, <sup>b,c</sup> %           3e         99 (96)           3e         65 (70)           3e         20 (46)           3e         23 (32)	broduct         yield, b, c %         Substrate           3e         99 (96)         4a           3e         65 (70)         5a           3e         20 (46)         6a           3e         23 (32)         6a	product         yield, <sup>b,c</sup> %         Substrate         product           3e         99 (96)         4a         4b           3e         65 (70)         5a         5b           3e         20 (46)         6a         6b           3e         23 (32)         6a         6b

<sup>a</sup> Experimental conditions: starting concentration of substrate was 0.2M; 1.5 equiv. of silane 2; AIBN (10%); 2h at 80°C. <sup>b</sup> GC yields. <sup>c</sup> Reaction performed in nonane (toluene). <sup>d</sup> Isolated yields.

The efficiency of the deoxygenation reaction via the phenyl thionocarbonates was further tested with compounds **4a**, **5a**, and **6a**.<sup>14</sup> The isolated yields are also reported in Table 1.



In order to quantify the observed reactivity of 2 and to provide a rate constant for H atom abstraction from this silane by an alkyl radical, we utilized a free-radical clock<sup>15</sup> devised and calibrated in our laboratory.<sup>16</sup> This indirect competition method is outlined in Scheme 1 and under pseudo-first order conditions follows the relation:

$$[8]/[9] = 1/K_{eq} + k_{H}/k_{d}[R_{3}SiH]$$
(2)

The quantities of 8 and 9 were obtained by GC analysis, following the thermally initiated reaction, and by using an internal standard. The ratio [8]/[9] varied in the expected manner with a change in the silane concentration. The mean value of  $k_H/k_d = 2.46$  at 100°C was obtained from 4 different silane concentrations according to eq. 2. At the same temperature for (TMS)<sub>3</sub>SiH a value of  $k_H/k_d = 5.78$  has been measured,<sup>16</sup> which indicates that the  $k_H$  for (TMS)<sub>3</sub>SiH is 2.35 times faster than the  $k_H$  for 2. Taking  $k_H=6.0 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$  at 100°C for (TMS)<sub>3</sub>SiH,<sup>17</sup> we calculated  $k_H=2.6 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$  at the same temperature for 2.

## Scheme 1



The rate constant for the reaction of primary alkyl radicals with Ph<sub>2</sub>SiH<sub>2</sub> is known to be  $5.6\times10^4$  M<sup>-1</sup>s<sup>-1</sup> at 110 °C.<sup>18</sup> Furthermore, taking into account the statistical number of hydrogens abstracted the rate constant values of  $2.8\times10^4$  M<sup>-1</sup>s<sup>-1</sup> for primary alkyl radical with Ph<sub>2</sub>SiH<sub>2</sub> and  $6.4\times10^4$  M<sup>-1</sup>s<sup>-1</sup> for secondary alkyl radical with 2 (relative rates per H atom) are obtained. The reason for this increase in the reactivity of 2 when compared with the structurally related Ph<sub>2</sub>SiH<sub>2</sub> (even for a less reactive alkyl radical)<sup>19</sup> is unknown. An extra stabilization of the silyl radical, induced either by a transannular interaction of the vicinal Si substituent in 2 or by flattening the radical center due to the ring constraint, may be responsible for the observed results.

In summary we have shown that 2 is a synthetically useful reagent for the radical deoxygenation of phenyl thionocarbonates, and that it exhibits a remarkable reactivity when compared with the related diphenylsilane, which allows it to support long radical chains and react under mild conditions. The particular spectrum of reactivity exhibited by this silane is currently under investigation.

Acknowledgement. We thank Dr. Marco Lucarini (Università di Bologna) for helpful discussions. Financial support from the Progetto Strategico del CNR "Tecnologie Chimiche Innovative" is gratefully acknowledged. T. G. wishes to thank Ciba-Geigy AG for a grant.

## **References and Notes**

- 1. Visiting Scientist. Permanent Address: Dipartimento di Chimica Organica e Biologica, Università di Napoli, Via Mezzocannone 16, 80134 Napoli, Italy
- 2. Barton, D. H. R.; McCombie, S. W. J. Chem. Soc. Perkins Trans. 1 1975, 1574.
- 3. Crich, D.; Quintero, L. Chem. Rev. 1989, 89, 1413.
- 4. Chatgilialoglu, C.; Ferreri, C. Res. Chem. Intermed. 1993, 19, 755.
- 5. Chatgilialoglu, C. Acc. Chem. Res. 1992, 25, 188.
- 6. (a) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. Cs. *Tetrahedron Lett.* 1991, 32, 7187.
  (b) Chatgilialoglu, C.; Ferreri, C.; Lucarini, M. J. Org. Chem. 1993, 58, 249.
- (a) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. Cs. Synlett 1991, 435.
   (b) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. Cs. Tetrahedron 1993, 49, 2793.
- (a) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. Cs. *Tetrahedron Lett.* **1990**, *31*, 4681.
   (b) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. Cs. *Tetrahedron Lett.* **1991**, *32*, 2569.
- 9. Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. Cs. Tetrahedron 1993, 49, 7193.
- 10. Chatgilialoglu, C. Chem. Rev., in press.
- 11. Oba, M.; Nishiyama, K. J. Chem. Soc., Chem. Commun. 1994, 1703.
- Compound 2, also known as 9,10-dihydro-9,10-disilaanthracene or 9,10-disila-9,10-dihydroanthracene, has been prepared by the reaction of LiAlH4 with the corresponding tetrachloro derivative which was given as a gift from Prof. E. A. Chernyshev. For the original synthesis of compound 2, see: Chernyshev, E. A.; Komalenkov, N. G.; Shamshin, L. N.; Shchepinov, S. A. Zh. Obshch. Khim. 1971, 41, 843; J. Gen. Chem. USSR (Engl. Transl.) 1971, 41, 850.
- The usual starting derivatives, i.e. thionocarbonates (3a), xanthates (3b) and thiocarbonyl imidazolides (3c), have recently been extended to thioxocarbamates (3d). See: Oba, M.; Nishiyama, K. Tetrahedron 1994, 50, 10193.
- 14. Typical Procedure: To a stirred solution of 5a (100 mg, 0.19 mmol) and 2 (67 mg, 0.32 mmol) in cyclohexane (2 mL) deoxygenated by successive applications of vacuum and argon gas, a catalytic amount of AIBN (5 mg) was added and the solution was brought at 80 °C. After stirring for 1h at 80 °C the solvent was evaporated under reduced pressure and the residue was chromatographed (hexane) to yield 95 mg (85%) of cholestane 5b.
- 15. For reviews on free-radical clocks, see: (a) Newcomb, M. Tetrahedron 1993, 49, 1151. (b) Griller, D.; Ingold, K. U. Acc. Chem. Res. 1980, 13, 317.
- 16. Chatgilialoglu, C.; Ferreri, C.; Lucarini, M.; Zavitsas, A. Manuscript in preparation.
- 17. Chatgilialoglu, C.; Dickhaut, J.; Giese, B. J. Org. Chem. 1991, 56, 6399.
- 18. Ballestri, M.; Chatgilialoglu, C.; Guerra, M.; Guerrini, A.; Lucarini, M.; Seconi, G. J. Chem. Soc., Perkin Trans. 2 1993, 421.
- At 100°C, the rate constant of (TMS)<sub>3</sub>SiH with a primary alkyl radical is 3 times faster than with secondary alkyl radical.<sup>18</sup>

(Received in UK 15 March 1995; accepted 31 March 1995)