## Addition Reaction and Deoxygenation of Alcohols Using Isothiocyanates and Triethylsilane-DTBP

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Abstract: Alcohols were found to be deoxygenated through treatment with isothiocyanates giving thionocarbamates, followed by reduction with triethylsilane.

The deoxygenation of alcohols via their derivatives under radical conditions has been widely studied by many groups.<sup>1</sup> Among the derivatizing reagents, phenyl chlorothionocarbamate<sup>2</sup> and diimidazolyl thioketone<sup>3</sup> are well known to be useful for the deoxygenation of alcohols. However, these reagents are relatively expensive or there are some difficulties in preparation, and tributylstannane should be used as a hydrogen donor in these reactions. The use of silicon hydrides instead of tin hydrides seems to be more attractive because of elimination of toxicity and waste problems, but there are only a few reports concerning a silicon hydride-reduction.<sup>4</sup> In this communication, we would like to report a new type of deoxygenation reaction, which consists of an addition of the alcohols to ethyl, phenyl, benzyl, and trimethylsilylmethyl<sup>5</sup> isothiocyanates (1a-1d) to give the corresponding thionocarbamates 2a-2d, and a reduction of 2 with triethylsilane under radical conditions to afford the deoxygenated product. The procedure using triethyldeuteriosilane was found to be applicable to a regioselective deoxydeuteration of alcohols.

The addition of alcohols to 1 was carried out as follows: an alcohol (ROH) was azeotropically converted into the alkoxide (ROSnBu<sub>3</sub>) by bis(tributyltin)oxide (1 equiv.) in refluxing toluene for 24 h, followed by an addition of 1 (2 equiv.), and then the mixture was kept at 60 °C for 20 h.<sup>6</sup> The thionocarbamates 2 were obtained through column chromatography on silica gel (eluted by benzene) in excellent yields. The addition reaction was not promoted by an acid, *i.e. p*-toluenesufonic acid, which catalyzes the addition of an alcohol to an isocyanate. The results are summarized in the Table. The addition could be applied to not only primary but also secondary alcohols. With 1-decanol, **1a**, **1b**, **1c**, and **1d** gave 1-decyl N-ethylthionocarbamate (**2ax**), 1-decyl N-phenylthionocarbamate (**2bx**), 1-decyl N-benzylthionocarbamate (**2cx**), and 1-decyl N-trimethylsilylmethylthionocarbamate (**2dx**) in 90, 75, 72, and 80% yields, respectively (runs 1, 3, 7, and 9). With 2-decanol, these isothiocyanates **1** afforded the corresponding 2-decyl thionocarbamates **2ay**, **2by**, **2cy**, and **2dy** in 94, 81, 94, and 70% yields (runs 2, 4, 8, and 10). All products gave satisfactory results in elemental or high-resolution mass spectrometric analyses. It was confirmed by nmr spectroscopic analyses that thiol carbamate, a rearranged isomer, was not involved in 2 at all under the conditions used.

ROH + R'NCS ROC(S)NHR' 1 2 a, R'=Et; b, R'=Ph; c, R'=PhCH<sub>2</sub>; d, R'=Me<sub>3</sub>SiCH<sub>2</sub> x, R=CH<sub>3</sub>(CH<sub>2</sub>)<sub>9</sub>; y, R=CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>CH(CH<sub>3</sub>); z, R=p-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>

Run	RNCS	Alcohol <sup>2</sup>	2/%	Hydrogen Donor <sup>3</sup>	Temp/°C	Deoxygenated Product/% <sup>4</sup>	Alcohol
1	1a	1-Dec	90	Si	140	70 (95)	
2		2-Dec	94	Si	140	42 (90)	
3	1b	1-Dec	75	Si	140	67 (95)	
4		2-Dec	81	Si	140	52 (81)	
5		2-Dec		Si	110	(60)	
6		2-Dec		Si	80	(0)	
7	1 c	1-Dec	72	Si	140	6	
8		2-Dec	94	Si	140	1	
9	1 d	1-Dec	80	Si	140	88	trace
10		2-Dec	70	Si	140	85 (90)	3
11		2-Dec		Si	140	(65) <sup>5</sup>	
1 <b>2</b>		2-Dec		Si	110	64	
13		2-Dec		Sn	140	7	49
14	р-М	leOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	75	Si	140	39 <sup>6</sup>	6

Table. Yields of Thionocarbamate 2 and Deoxygenated Product.<sup>1</sup>

<sup>1</sup> For a deoxygenation reaction, 0.05 M solution in benzene was heated in a sealed tube. <sup>2</sup> 1-Dec, 1-decanol; 2-Dec, 2-decanol. <sup>3</sup> Si, Et<sub>3</sub>SiH; Sn, *n*-Bu<sub>3</sub>SnH. <sup>4</sup> The isolated yields. The yields determined by vpc are also shown in parentheses. <sup>5</sup> The yield was obtained from 0.5 M solution. <sup>6</sup> 1,2-Bis(*p*-methoxyphenyl)ethane was obtained in a 21% of yield.

A reduction of the thionocarbamates 2 with triethylsilane or tributylstannane in benzene (0.05 M) was carried out at 140, 110, or 80 °C for 21 or 48 h in a sealed tube using a catalytic amount (10 mol%) of di-t-butyl peroxide (DTBP) or benzoyl peroxide (BPO) as an initiator. The isolated yields of deoxygenated compounds are also listed in the Table and the yields determined by vpc are shown in parentheses. From the reactions of 1and 2-decyl thionocarbamates 2ax, 2ay, 2bx, 2by, 2dx, and 2dy with triethylsilane, decane was obtained in moderate to high yields (runs 1, 2, 3, 4, 9, and 10) but a similar treatment of the corresponding N-benzylthionocarbamates 2cx and 2cy gave decane only in lower yields (runs 7 and 8). The inverse concentration dependence was observed for the yield of the deoxygenated product (run 11). When a reaction of 2by or 2dy with Et<sub>3</sub>SiH was carried out at 110 °C for 48h, decane was obtained but in lower yields (runs 5 and 12). The reaction of 2by with Et<sub>3</sub>SiH-BPO in refluxed benzene gave no decane and the starting material was quantitatively recovered (run 6). In contrast to the reported methods,<sup>2, 3</sup> a treatment of 2dy with tributylstannane gave decane only in a 7% yield together with 2-decanol (49%) (run 13). The reaction of *p*-methoxybenzyl trimethylsilylmethylthionocarbamate (2dz) with triethylsilane gave 1,2-bis(*p*-methoxyphenyl)ethane (21%), *p*-methoxybenzyl alcohol (6%), and the starting material (4%) along with *p*-methoxytoluene (39%) (run 14). From these findings, the reaction pathway was postulated as similar as the Barton-McCombie theory as follows:



R=1-C<sub>10</sub>H<sub>21</sub>, 2-C<sub>10</sub>H<sub>21</sub>; R'=Et, Ph, PhCH<sub>2</sub>, Me<sub>3</sub>SiCH<sub>2</sub>; M=Et<sub>3</sub>Si, n-Bu<sub>3</sub>Sn

In our case,  $\beta$ -elimination (eq 2) and hydrogen abstraction (eq 3) of a radical adduct I would be competitive, mainly depending upon the bond dissociation energies of metal-hydrogen bonding (M-H). With triethylsilane,  $\beta$ -elimination occurs predominantly to give R radical as the energy of silicon-hydrogen bonding is larger than that of tin-hydrogen bonding. Consequently, the reaction of the thionocarbamate 2dy with tributylstannane gave decane as a minor product and gave 2-decanol, which was considered to be a hydrolyzed product of II during the work-up, as a major product through hydrogen abstraction (eq 3). On 2cx and 2cy,  $\beta$ -elimination prefers to give R' radical rather than R radical because of the stability of benzyl radical.

In order to investigate the scope and the limitation of these reactions, we tried to examine a deoxygenation of cholest-5-en- $3\beta$ -ol (3) into cholest-5-ene (4). With 1a, 1b, and 1d, 3 gave the corresponding adducts in 70, 80, and 60% yields, and the adducts afforded 4 in 65, 65, and 50% yields, respectively. From an adduct of 1-dodecanol, 2-dodecanol, and 3 using triethyldeuteriosilane (Et<sub>3</sub>SiD), 1-deuteriododecane, 2-deuteriododecane, and 3-deuteriocholest-5-ene were regioselectively obtained in 90, 70, and 45% yields, respectively.

The structures of these compounds were confirmed by spectroscopic analyses<sup>7</sup> but the stereochemistry of the latter two has not been decided yet.



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## **References and Footnotes**

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- <sup>13</sup>C NMR spectra of deuteriododecanes are as follows: Dodecane-1-d; δ=13.45 (t, J=19.2 Hz), 14.05, 22.80, 29.51, 29.82, 29.86, and 32.09. Dodecane-2-d; δ=14.05, 22.38 (t, J=19.2 Hz), 22.78, 29.49, 29.79, 29.83 and 32.06.

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3748