## **RADICAL MONO- AND DIDEOXYGENATIONS WITH THE TRIETHYLSILANE + BENZOYL PEROXIDE SYSTEM.**

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**Abstract:** Thionocarbonates and xanthates of primary and secondary alcohols, as well as dixanthates of vic-diols can easily be deoxygenated to the corresponding hydrocarbons or olefins with triethylsilane and benzoyl peroxide in high-yielding radical reactions.

Deoxygenation of primary and secondary alcohols, especially nucleosides, antibiotics and carbohydrates is a never ending challenge in Organic Synthesis. Therefore, efficient and mild radical methods, compatible with often sensitive functional groups and ring systems are needed. The original Barton-McCombie reaction provided a solution to this problem for secondary alcohols<sup>1</sup>. Later the deoxygenation of primary and tertiary alcohols has also been solved this way<sup>2</sup>, <sup>3</sup>.

$$\begin{array}{ccccccccc} S & & & & SX & & & O \\ I & & X & & I & & & \\ R-O-C-R' & & & & & R' + & X-S-C-R' & & & & \\ \end{array}$$

There are many known applications of these reactions<sup>4</sup>. However, the use of tributyltin hydride presents problems related to price, tin residues, toxic waste, etc. Therefore, various attempts have been made to replace tin hydrides. The use of silicon hydrides seems to be attractive because of the relatively low molecular weight and elimination of toxicity and waste problems. The only problem remaining is, whether the silicon-hydrogen bond of a given silane is weak enough to make it possible to generate the corresponding silicon radical needed to carry the radical chain.

We have shown recently, that both the thiocarbonylation and the reduction steps can be modified thereby increasing the effectiveness of the original procedure. In addition to the originally employed xanthates, thionobenzoates<sup>1</sup> and selenobenzoates<sup>1,5</sup> a series of new derivatizing agents have been used recently. Thus, Robins has introduced phenyl chlorothionoformate<sup>6</sup> for derivatizing secondary alcohols. The corresponding methoxythiocarbonyl<sup>7</sup>, imidazolylthiocarbonyl<sup>1,8</sup> and 4-methylphenoxy-thiocarbonyl<sup>9</sup> derivatives of various alcohols have also been deoxygenated by radical methods. We have found that substituted chlorothionoformates (pentafluorophenyl-<sup>10</sup>, 2,4,6-trichlorophenyl-<sup>10</sup> and 4-fluorophenyl-<sup>11</sup>) gave good results both in the acylation and deoxygenation steps (occasionally carried out as a one-pot procedure).

Various silanes, especially tris(trimethylsilyl)silane, have replaced tributyltin hydride effectively<sup>12</sup>. We have found that the commercially available phenylsilanes (phenylsilane<sup>13</sup>, diphenylsilane<sup>11,14</sup> and triphenylsilane<sup>15</sup>) work well in radical deoxygenations as hydrogen atom donors and chain carriers. Although

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simple alkylsilanes have a relatively strong Si-H bond<sup>16</sup>, these compounds can still be used in radical deoxygenation reactions<sup>17, 18</sup>. Roberts and co-workers described the use of triethylsilane in these radical deoxygenations by polarity reversal catalysis<sup>18</sup>.

We now report that deoxygenations of xanthates and 4-fluorophenyl thionocarbonates can be achieved in neat triethylsilane solutions provided that effective initiation is maintained by the portionwise addition of benzoyl peroxide (Scheme 1, Table 1). The yields are in the range of 82-100% (Table 1) and the reaction conditions are well tolerated by various Natural Products (Scheme 1). The same method can also be used to transform vicdixanthates into olefins (Table 1, entries **4b** and **6b**). Product analysis (GC-MS) shows that the radical reaction follows the usual pathway<sup>19</sup>, similar to the one found in the case of radical deoxygenations with tributyltin hydride<sup>20</sup>.

Substrate	Product	Benzoyl peroxide (eq.)	Reaction time (min.)	Yicld (%)
1b	ld	1	150	96 <sup>3</sup>
1c	ld	1	150	89ª
2Ъ	2c	0.6	90	93 <sup>b</sup>
3b	3c	0.8	120	96 <sup>a</sup>
4b	5	0.6	90	100 <sup>a</sup>
6b	7	0.8	120	82 <sup>b</sup>

 Table 1
 Radical deoxygenation of primary and secondary alcohols and vic-diols with triethylsilane and benzoyl peroxide.

<sup>a</sup> determined by <sup>1</sup>H NMR <sup>b</sup> preparative yield

The presence of triethylsilyl benzoate, however, indicates that benzoyl peroxide is not only the source of the initiator benzoyloxy radicals, but also a trap for the triethylsilyl radicals. This finding explains the observation that relatively high amounts of benzoyl peroxide are needed (Scheme 2). Thus, the reaction of benzoyl peroxide **8** with boiling triethylsilane **13** gives benzene **16** (30%), triethylsilyl benzoate **11** (31%) and benzoic acid **20** (43%) (determined by <sup>1</sup>H NMR) in accordance with Scheme 2. In the presence of a xanthate, reaction of the phenyl radical **14** with the thiocarbonyl group of **15** can also be expected as a competing minor pathway<sup>21</sup>. (18, R' = SMe, 6% isolated yield). The excess triethylsilane can be recovered by simple distillation and the deoxygenated products isolated by crystallization or chromatography on a silica column. Our findings demonstrate that the triethylsilane + benzoyl peroxide system is a cheap and simple one for the high-yielding deoxygenation of primary and secondary alcohols.

**Typical procedure:** To the starting thionocarbonate **2b** (217 mg, 0.4 mmol) triethylsilane (3 ml, 18.8 mmol) was added under argon. Then the solution was brought to the boil and treated with benzoyl peroxide (19.4 mg, 0.08 mmol) at 30 minutes intervals. The reaction was monitored by tlc. When the reaction was complete (Table 1) the solvent was evaporated in vacuum and the hydrocarbon isolated by column chromatography on silica gel (eluent: hexanes) giving 138 mg (93%) of **2c**.



**a**:  $\mathbf{R} = \mathbf{OH}$ **b**:  $\mathbf{R} = \mathbf{OCSMe}$ 

Scheme 1



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