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ON THE MECHANISM OF DEOXYGENATION OF SECONDARY ALCOHOLS BY TIN HYDRIDE REDUCTION OF METHYL XANTHATES AND OTHER THIOCARBONYL DERIVATIVES

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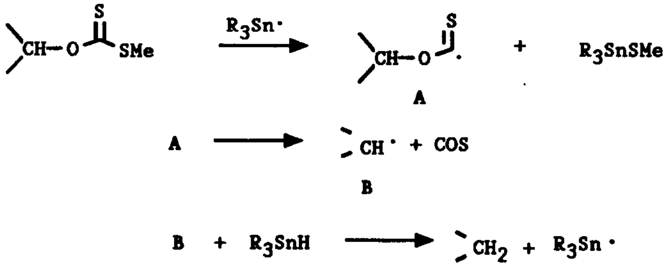
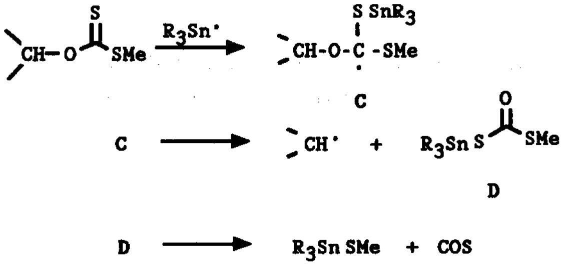
Abstract. The room temperature deoxygenation of xanthates and thionocarbonates using $(n\text{-Bu})_3\text{Sn-H}$ - Et_3B - air has been studied, especially with ^{119}Sn N.M.R. spectroscopy. The original conception of tin radical attack on thiocarbonyl is confirmed.

In 1984 Barker and Beckwith[1] concluded that the well-known tin hydride reduction[2] of the methyl xanthates of secondary alcohols to the corresponding deoxy compounds might involve tin radical attack on the -SMe function (Scheme 1), rather than the hitherto accepted attack on thiocarbonyl (Scheme 2). There have been arguments in favour of Scheme 2.[3,4] However, Forbes and Zard[5], in a seminal contribution, have recently shown that radical **A** (Scheme 1), when synthesized by irradiation of a xanthic anhydride, rapidly loses COS at room temperature. Furthermore, Oshima and his colleagues[6] have recently shown that methyl xanthates react with $(n\text{-Bu})_3\text{SnH-Et}_3\text{B}$ at room temperature to give a smooth deoxygenation. It seemed to us that the time was ripe to investigate again the mechanism of methyl xanthate deoxygenation, especially using ^{119}Sn NMR spectroscopy.



Scheme 1

We selected three thiocarbonyl derivatives **1a**, **1b** and **1c** for investigation, where R is the cyclododecyl residue. As expected, none of these compounds on admixture with $(n\text{-Bu})_3\text{SnH}$ and Et_3B in hexane at room temperature under oxygen-free, dry argon showed any sign of reaction (IR, ^{1}H, ^{11}B, ^{13}C, ^{119}Sn NMR).[7]



Scheme 2

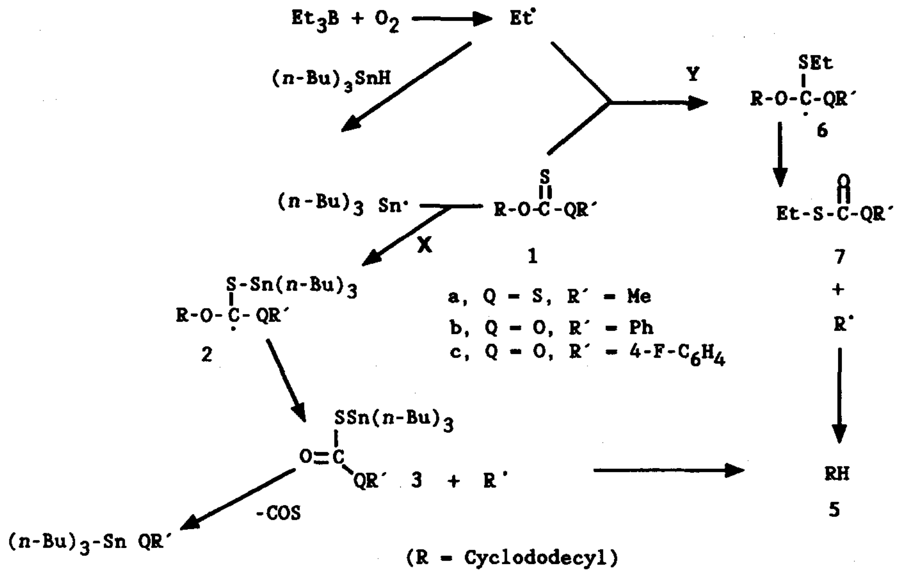
However, the reaction started when ethyl radical formation was induced by a controlled injection of air into the septum sealed flask.[6,8] Methyl xanthate **1a** (1 equiv.) reacted with (*n*-Bu)$_3$SnH-Et$_3$B (1.1 equiv. each) to give at room temperature **5** (90%) and unchanged **1a** (10%). Two additional products were **4a** (75%) and **7a** (13%).

If Scheme 1 were correct, the intermediate **3a** would not exist. However, if Scheme 2 were true, then intermediate **3a** should be detectable if the temperature were low enough. Variable temperature ^{119}Sn NMR proved to be a valuable technique for detecting **3a**. At -20° the above described experiment was repeated. An intermediate was clearly observed at 66 ppm in toluene-CD$_3$CN (or at 60 ppm in toluene-toluene-D$_8$). This was formed rapidly (10 min.) or slowly (2 hr.) depending on the amount of air injected. At -20° it was stable. Warming the reaction mixture to +20° for 90 mins. caused the disappearance of the intermediate peak at 66 ppm and the development of a new peak at 83-84 ppm identical with the peak shown by an authentic specimen[9] of **4a**. Since the intermediate at -20° is stable, but changes to **4a** on warming, it must be **3a**. Kinetic experiments at -20° showed that the formation **3a** was proportional to the disappearance of the (*n*-Bu)$_3$SnH.

We propose that the deoxygenation of **1a** proceeds as in Scheme 3 with a major pathway **X** involving tin radicals and a minor pathway **Y** which uses Et radicals. The former pathway has radical **2a**, intermediate **3a**, and stable products **4a** and **5**. The minor pathway **Y** has radical **6a**, stable product **7a** and, of course, **5**.

When the tin hydride is omitted, ethyl radicals are generated as before and **1a** reacts by pathway **Y** to give **5** (62%), cyclododecene (12%), bicyclododecyl (9%) and a trace of cyclododecanone (4%). The expected ethyl derivative **7a** was also formed (91%). The reaction is not as clean as the tin hydride reduction pathway **X**.

The analogous deoxygenation[10] of thiono-carbonates **1b** and **1c** were also studied using ^{119}Sn NMR spectroscopy. Again the (*n*-Bu)$_3$SnH - Et$_3$B - air system was used since it works well at -20°. At this temperature, tin



Scheme 3[14]

containing intermediates **3b** and **3c** appeared at about 66 ppm. in toluene/toluene-D. This peak increased with time. Intermediates **3b** and **3c** were more stable at 0° than **3a**. However, they decomposed at 20° to give a singlet at 106 ppm[11] for **4b** and **4c**. On standing for several weeks both compounds gave $[(n\text{-Bu})_3Sn]_2O$ with a peak at 82-83 ppm in agreement with an authentic specimen.[12]

In our previous studies[3] of the deoxygenation reaction using methyl xanthate derivatives, we had concluded that as the temperature was lowered from about 80° the deoxygenation intermediate radicals like **2** were partitioned between fragmentation and further reduction to furnish eventually, after work-up, thiols of type RO-CH$_2$SH. Clearly from the work now reported, any radicals like **2** rapidly fragment and therefore the thiol reduction product must be formed by a different hydride transfer type reduction.

In agreement, when cholestanol methyl xanthate was heated under reflux with $(n\text{-Bu})_3SnH$ in benzene without any initiator, the RO-CH$_2$SH product isolated before[3] was formed (55%), along with the deoxygenated product cholestane (31%), no doubt formed by radical fragmentation.

In conclusion, this article shows that the application of ^{119}Sn NMR spectroscopy solves easily a sophisticated problem in radical chemistry.[13]

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7. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-200 NMR Spectrometer in $CDCl_3$ or C_6D_6 solutions at ambient temperature. (20°C). TMS was usd as an internal reference. 64 MHz ^{11}B NMR spectra were obtained using C_6H_6/C_6D_6 solutions on a Varian XL-400 NMR spectrometer, referenced to external $BF_3.Et_2O$ (δ=0.00 ppm). The samples were prepared under dry, oxygen-free argon prior to the addition of air. The 149 MHz ^{119}Sn NMR spectra were recorded on a Varian XL-400 NMR spectrometer referenced to external Me_4Sn (δ=0.00 ppm) and internal D. The 20°C experiments were run on samples dissolved in benzene/denzene-d_6 or toluene/toluene-d_8. The variable temperature measurements were done on samples dissolved in $EtOH/CD_3CN$, toluene/CD_3CN or toluene/toluene-d_8. (n-Bu)$_3$SnH absorbed at -89 ppm., (n-Bu)$_3$SnOSn(n-Bu)$_3$ at 83 ppm, n-Bu$_3$SnSMe at 82 ppm, (n-Bu)$_3$SnOPh at 106 ppm. For a collection of ^{119}Sn chemical shifts, see ref. 11.

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14. Compound **1c** gave satisfactory elemental analysis data. Its spectral properties (IR, ^{1}H and ^{13}C NMR) were in accordance with its structure.

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