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SYNTHESIS OF LACTONES BY INTRAMOLECULAR ADDITION OF ALKOXYTHIOCARBONYL FREE RADICALS TO ACETYLENES

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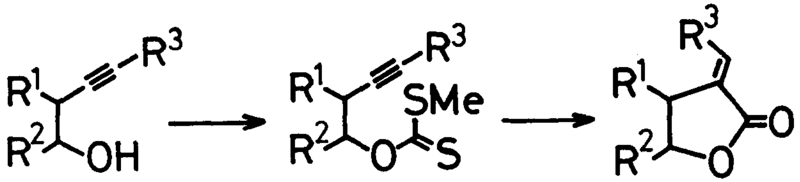
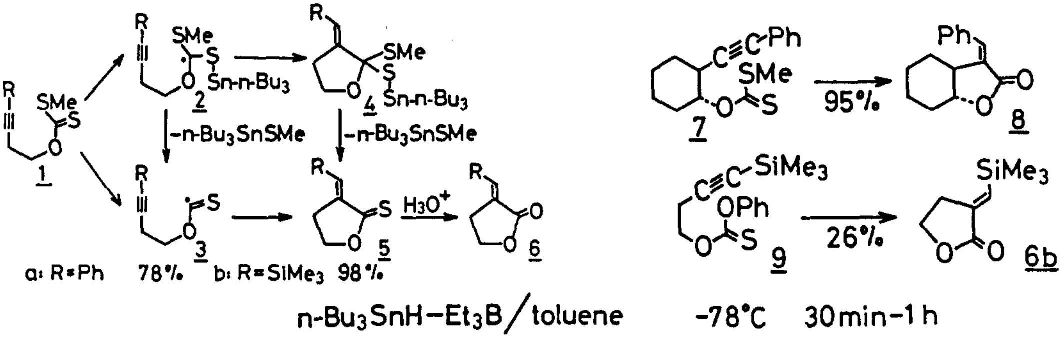
Summary: Lactones are obtained by treating dithiocarbonates of homopropargylic or homoallylic alcohols with n-Bu_3SnH-Et_3B.

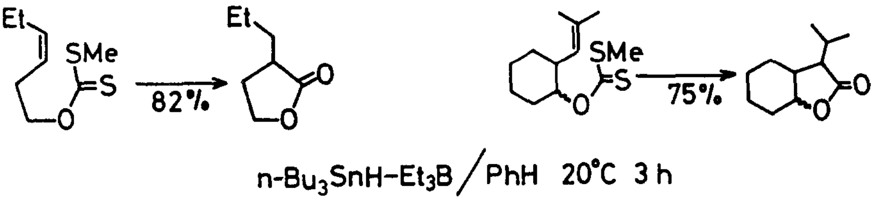
In a preceding paper[1] we have reported that the reduction of dithiocarbonates with n-Bu_3SnH-Et_3B easily provided the corresponding hydrocarbons. Here, we report that treatment of dithiocarbonates which have properly located triple or double bonds with n-Bu_3SnH-Et_3B gives lactones by intramolecular addition of alkoxythiocarbonyl free radicals to the multiple bonds.



A toluene solution of n-Bu_3SnH (0.5 M, 2.2 ml, 1.1 mmol) was added dropwise to a solution of Et_3B (1.0 M hexane solution, 1.1 ml, 1.1 mmol) and dithiocarbonate **1a**[2] (0.43 g, 1.0 mmol) in toluene (20 ml) at -78 °C under an argon atmosphere. The resulting mixture was stirred for 30 min at -78 °C and poured into 1N HCl. Extractive workup followed by purification by preparative tlc on silica gel gave α-benzylidene-γ-butyrolactone **6a**[3] (0.14 g) in 78% yield. The product was not contaminated by benzylthionolactone or benzyllactone (<1%), which is generated by reduction of initially formed benzylidenethionolactone with n-Bu_3SnH under ordinary reaction conditions (AIBN, benzene reflux).[4,5] Generality and mildness of the reaction which employs readily available starting materials were shown by the following examples.[6] Dithiocarbonate **7**[7] derived from secondary alcohol also provided the desired lactone **8**[8] in good yield in preference to deoxygenation to hydrocarbon. The extension of this method to the preparation of lactone **6b**[9] from thiocarbonate **9** resulted in low yield.



Butyrolactones were also easily produced from dithiocarbonate derivatives of homoallylic alcohols.[10]



References and Notes

1. K. Nozaki, K. Oshima, and K. Utimoto, Tetrahedron Lett., preceding communication.
2. **1a**: Bp 97 °C (bath temp, 1.0 Torr); IR (neat) 2910, 1489, 1221, 1079, 970, 755, 690 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 2.59 (s, 3H), 2.93 (t, *J* = 7.0 Hz, 2H), 4.78 (t, *J* = 7.0 Hz, 2H), 7.25-7.50 (m, 5H). Found: C, 60.97; H, 5.05%. Calcd for $C_{12}H_{12}OS_2$: C, 60.98; H, 5.12%.
3. **6a**: E/Z = 94/6. I. Matsuda, S. Murata, and Y. Izumi, Bull. Chem. Soc. Jpn., **52**, 2389 (1979).
4. A. G. Angoh and D. L. J. Clive, J. Chem. Soc. Chem. Commun., **1985**, 980.
5. M. D. Bachi and E. Bosch, Tetrahedron Lett., **27**, 641 (1986).
6. Two radical intermediates **2** and **3** were proposed by Barton (D. H. R. Barton, D. Crich, A. Löbberding, and S. Z. Zard, Tetrahedron, **42**, 2329 (1986)) and Beckwith (P. J. Barker and A. L. J. Beckwith, J. Chem. Soc., Chem. Commun., **1984**, 683). Evaporation of the reaction mixture provided **5** which was converted into **6** upon workup (1N HCl).
7. **7**: Mp 61 °C (MeOH); IR (neat) 2926, 2858, 1487, 1440, 1253, 1225, 1055, 1037, 969, 760, 692 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.25-2.40 (m, 8H), 2.58 (s, 3H), 2.93-3.08 (m, 1H), 5.65-5.80 (m, 1H), 7.25-7.50 (m, 5H). Found: C, 66.47; H, 6.23%. Calcd for $C_{16}H_{18}OS_2$: C, 66.17; H, 6.25%.
8. **8**: pure *trans*-E isomer; IR (neat) 2932, 2858, 1759, 1257, 1227, 1206, 1188, 1120, 1093, 1015, 701 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 0.85-2.48 (m, 8H), 2.66-2.87 (m, 1H), 3.90-4.06 (m, 1H), 7.23-7.46 (m, 5H), 7.99 (d, *J* = 2.0 Hz, 1H). Physical data for *trans*-Z isomer have been reported in Ref. 3.
9. Desilylation of α-trimethylsilylmethylene-γ-lactone into α-methylene-γ-lactone has been reported. M. D. Bachi and E. Bosch, Tetrahedron Lett., **29**, 2581 (1988).
10. Financial support by the Ministry of Education, Science, and Culture of Japan (Grant-in-Aid for Scientific Research No. 63470074) is acknowledged.

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