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Novel Radical Chain Reactions Based on *O*-Alkyl Tin Dithiocarbonates

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Most of the recent applications of radical reactions to organic synthesis are based on tin hydride chemistry.[1] One of the limitations of such a system is that the last propagation step involves a fast, irreversible, hydrogen atom transfer.[2a,c] Not only is a potential means of introducing an extra functionality lost but the intervening steps (cyclizations, additions etc.) have to be fast in order to compete with premature hydrogen abstraction. In practice, either high dilution conditions are employed or the tin hydride is added very slowly to keep its concentration low. Another approach has involved the use of the rather expensive germanium hydrides[2b,c] or tris(trimethylsilyl)silane,[3] both of which are less efficient hydrogen donors. An important variant involves the use of allyltin derivatives to introduce an allyl group.[4] In this communication, we wish to introduce *O*-alkyl tin dithiocarbonates (xanthates) as reagents which circumvent both of these limitations.

Our conception, outlined in Scheme I, is based on the fact that addition of tin radicals onto the thiocarbonyl group of a xanthate is reversible.[5] Thus, starting from tin xanthate **1** as the source of stannyl radicals, it should be possible to generate a radical R• from a substrate RX. This radical can of course react with the tin xanthate reagent to give xanthate **3** by a series of reversible steps (path A) or it can be converted through cyclization, fragmentation, etc. (summarized as step B) into another radical R*•, which in turn reacts to give xanthate **4**. Both pathways propagate

Scheme I

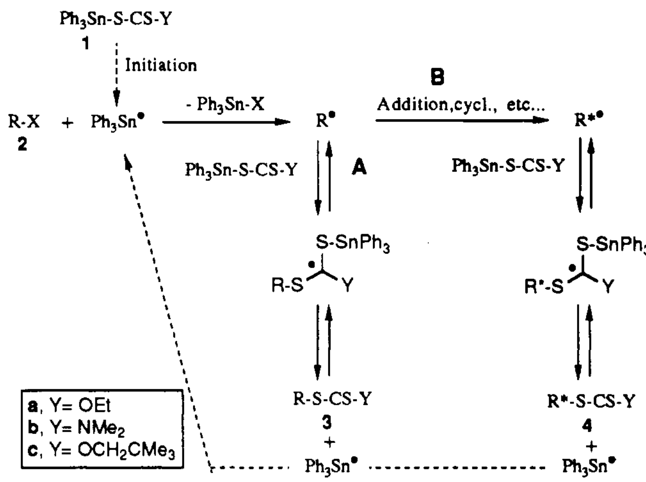

Table I. Reaction of Various RX Derivatives with Tin Dithiocarbonates

entry	RX	tin xanthate	additive	reaction time (initiator)[a]	product (yield, %)
1	**5**	**1a**	none	3 h, A	**6** (88)[b]
2	**7**	**1a**	none	4 h, A	**8** (67)[c]
3	**5**	**1a**	none	6 h, B	**6** (84)[b]
4	**7**	**1a**	none	6 h, B	**8** (55)[c]
5	**5**	**1b**	none	7 h, A	**9** (55)[b]
6	**5**	**1b**	none	10 h, B	**10** (24)[b]
7	**5**	**1c**	none	8 h, B	**11** (56)[b]
8	**5**	**1c**	$(Ph_3Sn)_2$	1 h, B	**11** (96)[b]
9	**5**	**1c**	$(Bu_3Sn)_2$	3 h, B	**11** (82)[b]
10	**12**	**1c**	none	10 h, B	**13** (55, 68[d])
11	**14**	**1c**	none	18 h, B	**15** (65)[e]
12	**16**	**1c**	$(Ph_3Sn)_2$	5 h, B	**17** (65)
13	**18**	**1c**	$(Ph_3Sn)_2$	2 h, B	**19** (80)
14	**20**	**1c**	$(Ph_3Sn)_2$	4 h, B	**19** (27, 48[d])
15	**21**	**1c**	$(Ph_3Sn)_2$	8 h, B	**22** (63)
16	**23**	**1c**	$(Ph_3Sn)_2$	3 h, B	**24** (25, 65[d])
17	**25**	**1c**	$(Ph_3Sn)_2$	15 h, B	**26** (79)
18	**27**	**1c**	$(Ph_3Sn)_2$	8 h, B	**28** (64, 80[d])

[a] A = initiation with 10 mol % (with respect to substrate) each of Bu_3SnH and AIBN; B = initiation with a 500-W tungsten halogen lamp. [b] 7:3 mixture of isomers. [c] 8:2 mixture of isomers. [d] Yield was based on recovered starting material. [e] 9:1 mixture of isomers.

the chain by regenerating the stannyl radical. One can, therefore, not only carry out the common radical reactions traditionally based on tin hydride chemistry but also introduce a very useful xanthate group into the end product **4**.[6] Moreover, as all of the steps involving transfer of the xanthate group are reversible, it should not be necessary to worry about high dilution, etc. in cases where one or more of the desired reactions of the intermediate carbon radical ("step B") are relatively slow, since one can always go back to the carbon radical through the action of stannyl radicals on xanthate **3** (reverse of path A).

These expectations were borne out in practice as shown by the following examples. Refluxing a solution of bromide **5** with *O*-ethyl triphenyltin xanthate **1a** in cyclohexane in the presence of a small amount of tributyltin hydride and AIBN as initiator resulted in the formation of bicyclic xanthate **6** in 88% yield. In a similar way, **8** was produced in 67% yield from **7**. Initiation of these reactions could be accomplished using visible light in comparable yields (Table I). The tin xanthate reagent **1a** is easily prepared[7a] from commercially available triphenyltin chloride and

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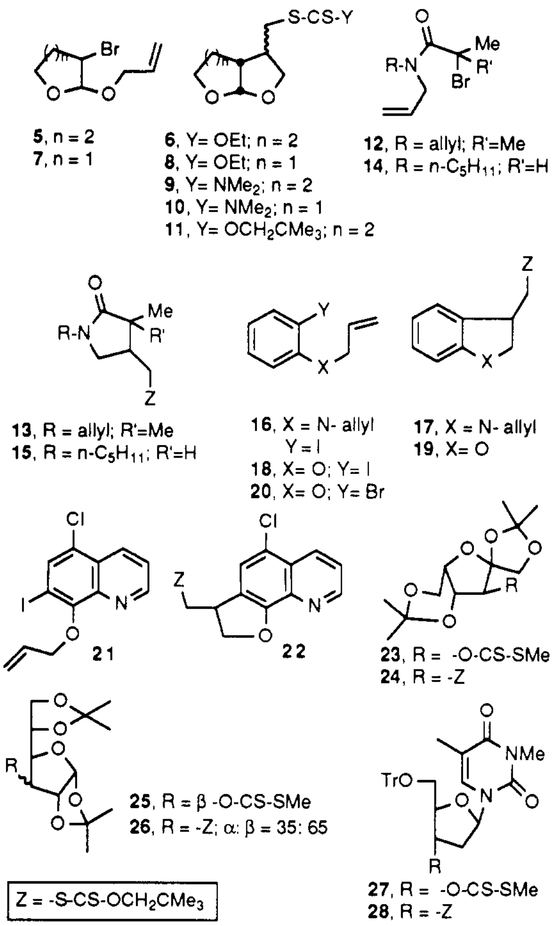
Chart I



potassium *O*-ethyl xanthate. However, it is a low-melting solid which does not keep well, resulting in erratic behavior in some of the experiments. The analogous dithiocarbamate derivative **1b**[7b] was more stable but much less reactive (see Table I, entries 5 and 6). In contrast, the neopentyltin xanthate **1c** turned out to be a stable and effective reagent, giving reproducible results. It is nicely crystalline (mp 94–96 °C) and easily made[7c] and kept. Moreover, we found that addition of a small amount (ca. 10 mol %) of hexabutylditin or, even better, hexaphenylditin increased the rate significantly,[7d] presumably by destroying traces of sulfur-containing impurities[8] or side products which can otherwise inhibit the chain reaction.

As shown in the table, a variety of typical radical reactions can be performed using this novel system. In the case of lactam formation (examples **13** and **15**), no need for high dilution or slow addition of the tin reagent is necessary, in contrast to similar stannane-mediated cyclizations.[9] As would be expected, aromatic bromides were much less reactive than the corresponding iodides (entries 13 and 14). It is also possible to convert an *O*-alkyl xanthate into an *S*-alkyl xanthate as illustrated by examples **24**, **26**, and **28** (entries 16–18) in what appears to be a promising and expedient route to thiosugars and thionucleosides. Some of these derivatives exhibit interesting biological activities and are not always easily accessible by conventional ionic reactions.[10] In the case of **26**, the two epimeric xanthates were shown to interconvert under the reaction conditions, indicating that the xanthate transfer is indeed a reversible process.

We believe that this approach adds a new dimension to tin-based radical methods. Furthermore, since the addition of silyl radicals onto a thiocarbonyl group has also been shown to be reversible,[4c] a similar process should be feasible with the corresponding silicon xanthates.

Acknowledgment. We thank Dr. B. Quiclet-Sire for a gift of tritylthymidine and Dr. J.-L. Fourrey for helpful discussions.

Registry No. 1a, 22703-09-9; **1b**, 1803-12-9; **1c**, 143037-51-8; **5**, 73746-50-6; **6** (isomer 1), 143037-52-9; **6** (isomer 2), 143119-80-6; **7**, 143037-46-1; **8** (isomer 1), 143037-53-0; **8** (isomer 2), 143119-81-7; **9** (isomer 1), 143037-54-1; **9** (isomer 2), 143119-82-8; **10** (isomer 1), 143037-55-2; **10** (isomer 2), 143119-83-9; **11** (isomer 1), 143037-56-3; **11** (isomer 2), 143119-84-0; **12**, 39089-47-9; **13**, 143037-57-4; **14**, 143037-47-2; *cis*-**15**, 143037-58-5; *trans*-**15**, 143037-59-6; **16**, 73396-92-6; **17**, 143037-60-9; **18**, 24892-63-5; **19**, 143037-61-0; **20**, 60333-75-7; **21**, 123552-78-3; **22**, 143037-62-1; **23**, 143037-48-3; **24**, 143037-63-2; **25**, 143037-49-4; α-**26**, 143037-64-3; β-**26**, 143037-65-4; **27**, 143037-50-7; **28**, 143037-66-5.

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Synthesis of an Equilateral Triangular Molybdenum Cluster Complex $[Mo_3(\mu_3\text{-}S)_2(\mu\text{-}S)_3(PMe_3)_6]$ with Eight Cluster Valence Electrons

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Several structural types of trinuclear molybdenum cluster complexes have been reported, and the relationship between their geometrical and electronic structures has been an important subject of intensive studies.[1] In the present communication, we report a new cluster complex $[Mo_3(\mu_3\text{-}S)_2(\mu\text{-}S)_3(PMe_3)_6]$ (I) containing a "Mo_3S_5" unit with two capping and three edge-bridging sulfur ligands. The unit is the first member of the series $Mo_{3n}S_{3n+2}$

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