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MECHANISM OF THE ADDITION OF TRIBUTYLTIN IODOACETATE TO ALKENES

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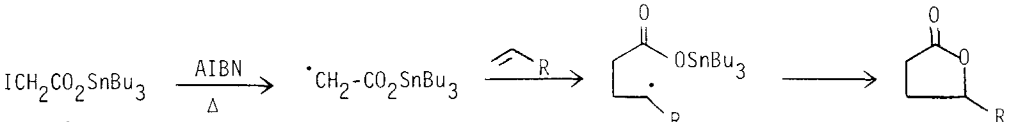
ABSTRACT: The mechanism of the formation of lactones by free radical additions of tri-n-butyltin iodoacetate to alkenes occurs through a two-step process: a homolytic addition of the ester (addition of $^{\bullet}CH_2-CO_2SnBu_3$, iodine transfer), followed by a fast ionic cyclization with elimination of tri-n-butyltin iodide.

The synthesis of γ-butyrolactones by free radical processes is an active research area. Heiba[1] initiated it using the manganic triacetate additions of acids to alkenes. Recently, Fristad[2] and Corey[3] have published important extensions of this basic reaction. Stork[4] and Ueno[5] used homolytic cyclizations of bromoketals, followed by oxidation of the cyclic compounds. Nikishin[6] offered a different free radical route to lactones. Burke[7] and Clive[8] have also reported clever approaches. Recently, we developed two different ways:

- Addition of tri-n-butylstannyl iodoesters to electron rich alkenes[9]:



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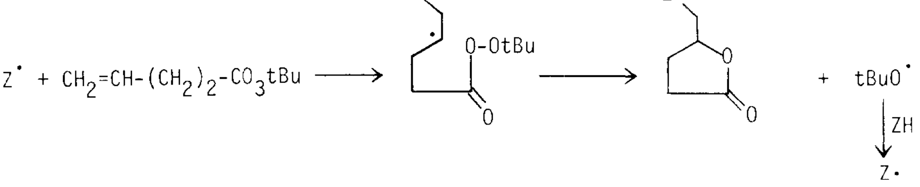
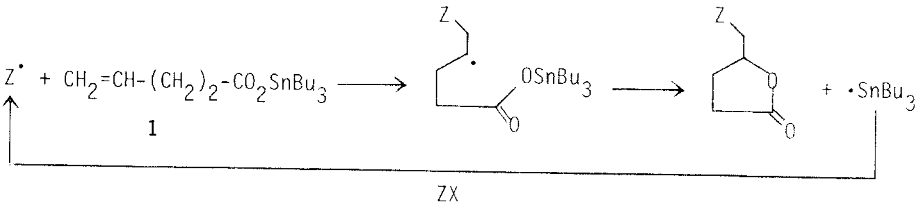
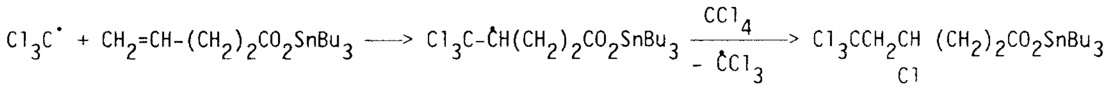
- Induced decomposition of γ-unsaturated peresters[10]:



Each of these two methods has its particular disadvantages, e.g., the first one cannot give 3,3-disubstituted lactones; in the second the radical chain carrier (t-butoxyl radical) has a very low selectivity in the hydrogen abstraction, giving in some cases several different radicals from ZH. The combination of both ideas suggested a novel strategy for the synthesis of lactones: the free radical addition of the appropriate halide ZX to a tri-n-butylstannyl ester containing an alkene subunit.

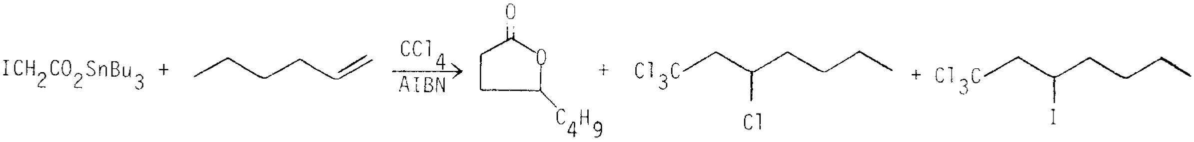


Carbon tetrachloride was a good choice for ZX. We performed its free radical addition to tri-n-butylstannyl pent-4-enoate, initiated by benzoyl peroxide (CCl_4/1/BP = 50/1/0,1). The reaction product was not the expected lactone but the direct adduct, isolated with a high yield (98%):



$$Cl_3C^{\bullet} + CH_2{=}CH\text{-}(CH_2)_2CO_2SnBu_3 \longrightarrow Cl_3C\text{-}\dot{C}H(CH_2)_2CO_2SnBu_3 \xrightarrow[-\ \dot{C}Cl_3]{CCl_4} Cl_3CCH_2\underset{Cl}{CH}\ (CH_2)_2CO_2SnBu_3$$

This experiment showed that the homolytic intramolecular substitution is a slower process than the chlorine abstraction to CCl_4 by a secondary alkyl radical; this suggested that Kraus' mechanism was incorrect. To see if 2 was obtained by the SHi process, we replaced the benzene, used as solvent in the Kraus experiment, by CCl_4. Thus, AIBN was thermally decomposed in a solution of tri-n-butyltin iodoacetate and 1-hexene in CCl_4.



2 (yield 34%)*

3

4 (21%)*

As 2 was obtained instead of the tri-n-butyltin chloroalkanoate, the formation of 2 by SHi must be precluded. Indeed, the rate of production of the lactone via the secondary alkyl radical is higher than its trapping by CCl_4, itself faster than the supposed homolytic displacement.

The byproducts 3 and 4 (ratio 3/4 = 1.6) came from the addition of trichloromethyl radicals to 1-hexene followed by an iodine or chlorine atom abstraction from the iodoester 1 and carbon tetrachloride. This observation led us to propose the following mechanism to explain the formation of the lactone:

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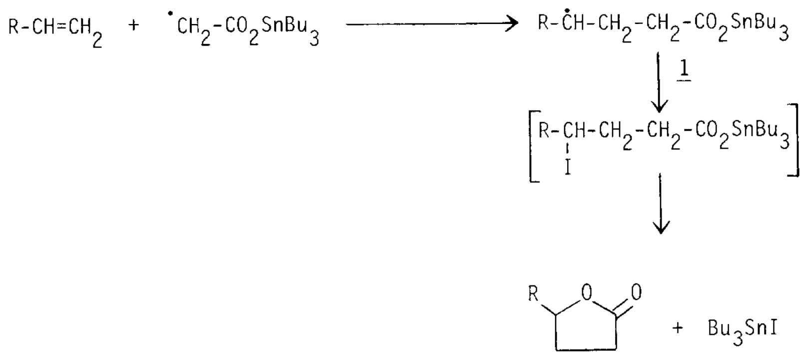
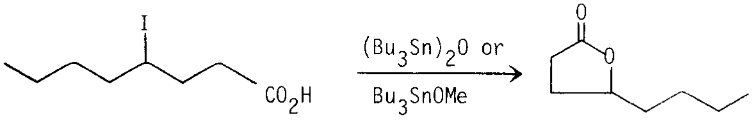
*Determined relatively to the starting iodoester.

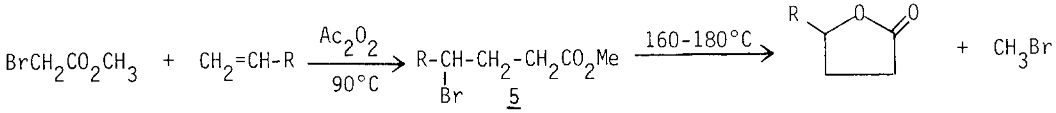


Several attempts to prepare and isolate tri-n-butylstannyl γ-iodesters were unsuccessful, the γ-lactone being the only product isolated.



This can be taken as a confirmation of the easy elimination of tri-n-butyltin iodide from the unstable γ-iodoester.

In the study of the free radical addition of bromoesters to alkenes Kharasch[11] reported that the 4-bromoesters 5 can be converted into the lactone simply by heating.



The replacement of the methyl by the tri-n-butylstannyl moiety increases the partial negative charge on the oxygen atom, making it much more nucleophilic. The change from bromine to iodine improves the leaving group. An analogous elimination has been previously invoked by one of us.[12] This may explain the facility of this elimination.

The discovery of this mechanism is a starting point for the study of a new class of free radical additions which lead to unstable compounds that are converted into products via an ionic process.

References and Notes

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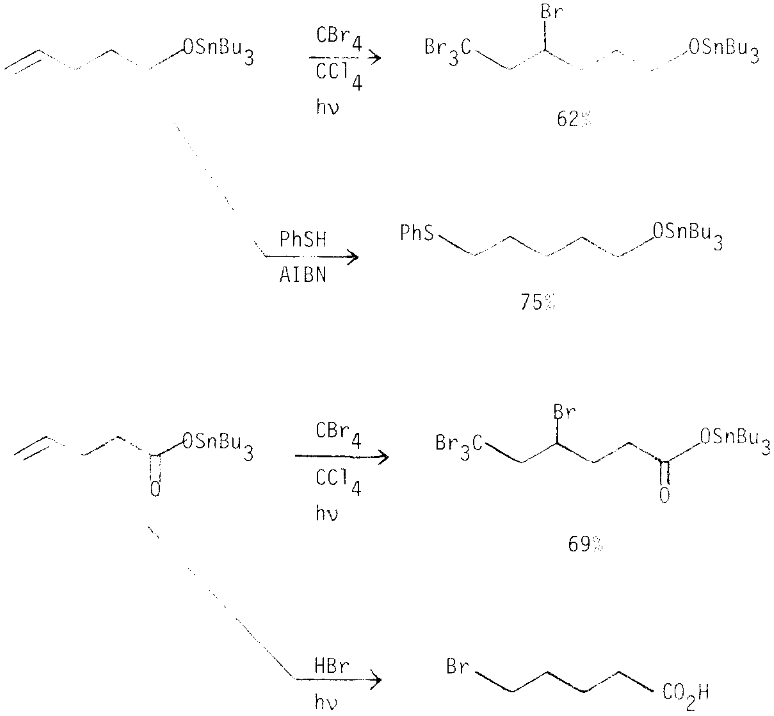

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