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SYNTHESIS OF α-ALKYLIDENE-γ-LACTONES BY INTRAMOLECULAR ADDITION OF ALKOXYCARBONYL FREE-RADICALS TO ACETYLENES

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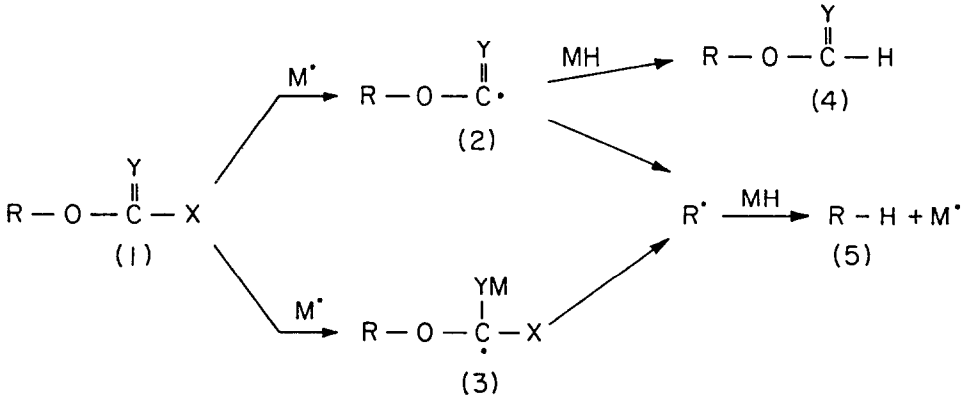
Abstract: α-Alkylidene-γ-lactones are obtained by treatment of chloroformate and selenocarbonate derivatives of homopropargylic alcohols with tri-n-butylstannane.

The free-radical reductive degradation of various carbonic acid derivatives (**1**) has been extensively used for the deoxygenation of alcohols.[1] The most useful, on the preparative scale, is the reaction of trialkylstannanes with dithiocarbonates,[2] thiocarbonylimidazolides,[2] thionocarbonates,[3,4] and selenocarbonates,[5] which lead to the corresponding desoxy products (**5**). Similar reductions of chloroformates with trialkylstannane[6,7] or trialkylsilanes[8] afford the corresponding formyl ester (**4**) and/or alkanes (**5**) depending on the nature of the substrate and the reaction conditions. Each of these reactions seems to follow one of the mechanisms displayed in Scheme I.[9,10]

Scheme I

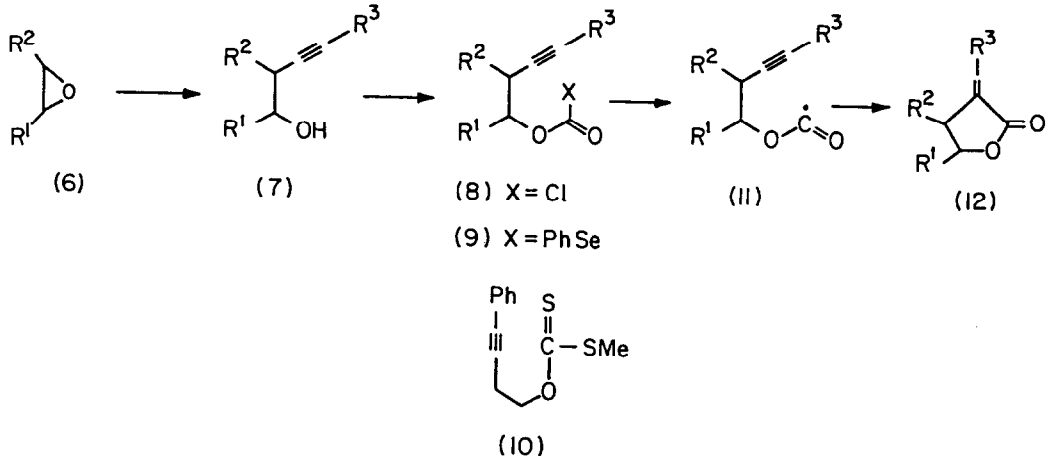


Y = O or S; X = Cl, OR', SR', SeR', or Imidazolide; M = R'''_3 Sn or R'''_3 Si

We postulated that, provided a multiple bond is properly positioned on the residue R of the carbonic acid derivative (**1**), the intermediate free-radical (**2**) or (**3**) will undergo intramolecular addition. The suitability of such a process for the construction of cyclic systems would require that the annulation efficiently compete with hydrogen abstraction leading to compounds (**4**) or with β-elimination of the intermediate radical (**3**).[11]

We now report on the successful application of this new methodology for the synthesis of α-alkylidene-γ-lactones. Compounds of type (**1**) were prepared by known procedures (Scheme II). Treatment of oxiranes (**6**) with lithium acetylides in the presence of boron trifluoride etherate afforded the corresponding 3-alkyn-1-ols (**7**),[12] which were converted (phosgene) into the chloroformates (**8**) and subsequently (PhSeH, pyridine) into the corresponding phenylselenocarbonates (**9**).[5] The dithiocarbonate (**10**) ($R^1 = R^2 = H$; $R^3 = Ph$) was obtained from the corresponding alcohol, CS_2 and MeI.[2b]

Scheme II

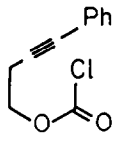
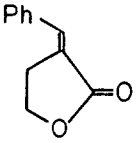
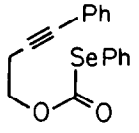
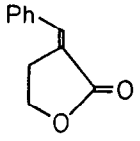
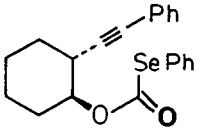
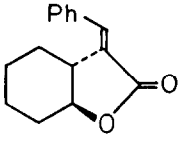
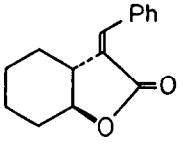
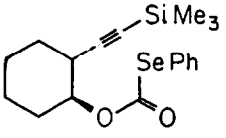
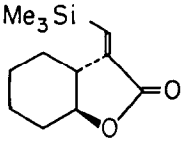
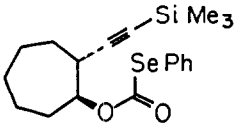
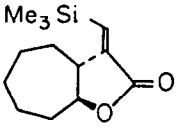
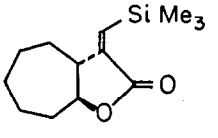
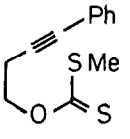
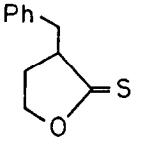


The table displays data on the free-radical cyclization of carbonic acid derivatives of homopropargylic alcohols. The radical source, tri-n-butylstannane and AIBN (azaisobutyronitrile), was gradually added (1.5-3 h) to the substrates (**8**)-(**10**). While the cyclization of chloroformates occurred in moderate yield (entry a), the conversion of the selenocarbonates into the corresponding lactones was practically quantitative (nmr, tlc) and their isolated yields were very high (entries b-e).

In a typical experiment (entry b) individual benzene solutions (10 ml each) of n-Bu_3SnH (0.9 mmol) and AIBN (0.085 mmol) were simultaneously added, during 2 h, to a boiling solution of the acetylenic selenocarbonate (**9**) ($R^1 = R^2 = H$; $R^3 = Ph$) (0.8 mmol) in benzene (60 ml). The crude product, obtained after evaporation of the solvent, consisted of (E)-α-benzylidene-γ-butyrolactone (quantitative; nmr, tlc) and tin derivatives. The pure lactone[13,14] was obtained (87%) by flash chromatography (silica gel; hexane-ethyl acetate), followed by fractionation between acetonitrile and hexane.

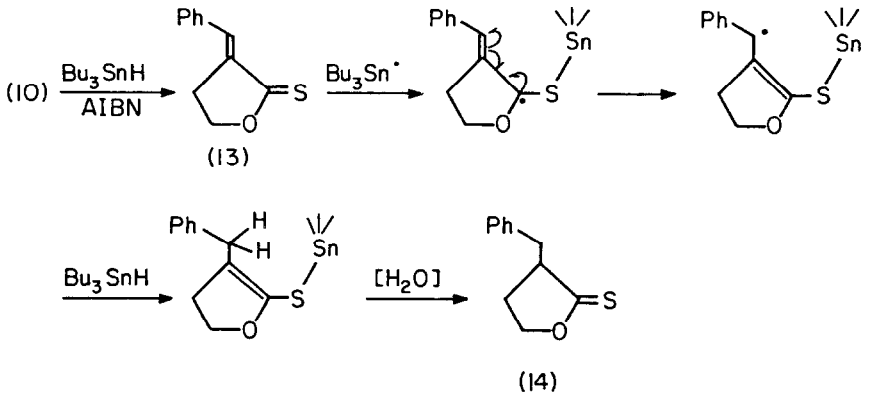
The reaction of the dithiocarbonate (**10**) took a different course (entry f). Full consumption of the starting material required a three-fold excess of n-Bu_3SnH, and the isolated cyclic product was found to be the benzylthionolactone (**14**) rather than the benzylidenethionolactone (**13**). A similar transformation was observed by Angoh and Clive on treatment of an acetylenic thiocarbonylimidazolide with Ph_3SnH.[15] Presumably the initially formed benzylidenethionolactone is further, and rapidly, reduced by n-Bu_3SnH as shown in Scheme III.

Table: The Reaction of Homopropargylic Derivatives of Carbonic Acids (**8**)-(**10**) with Tri-n-butylstannane and AIBN in Boiling Benzene

	Compounds type (8)-(10)	Products*	Yield** %	E/Z**
a			56	E
b			87	E
c		 	90	5/1
d		 	80	1/12
e		 	92	1/10
f			49	–

*See reference 14. **Based on isolated compounds

Scheme III



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