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INTRAMOLECULAR CYCLIZATION OF ALLYLIC PROPIOLATES MEDIATED BY THE ADDITION OF STANNYL RADICALS: A NEW SYNTHETIC ROUTE TO α-METHYLENE-γ-BUTYROLACTONES

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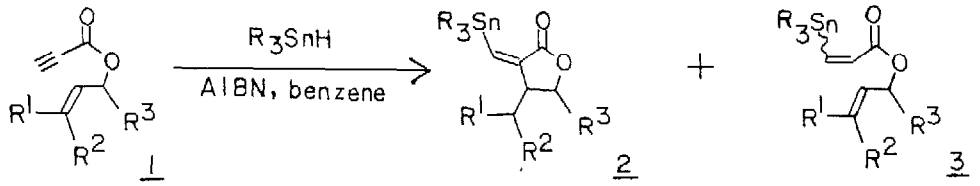
Summary: Allylic propiolates react with tributyl- or triphenylstannane to yield α-(stannyl)methylene-γ-butyrolactones. α-Methylene-γ-butyrolactones are easily prepared by destannylation.

Recently much attention was directed to the chemistry of vinyl radicals generated from alkynes.[1] We were intrigued by the possibility of cyclization of the vinyl radicals generated by the addition of stannyl radicals to allylic propiolates. Radicals generated from allylic haloacetates and tributylstannane are known to be immune to cyclization,[2] but reports on the reactivity of allylic α-acryloyl radicals have not yet been published.

Allylic propiolates were prepared from propiolic acid and allylic bromides.($NaHCO_3$, DMF, r.t., 20 hours) Allyl, crotyl, dimethylallyl propiolates (1a-c) reacted with triphenylstannane under radical conditions to produce moderate yield of γ-butyrolactones 2a-c in addition to the simple addition products 3a-c. Cyclohexenyl propiolate (1d) was primarily converted to 3d accompanied by relatively low yield of 2d. On the other hand, cinnamyl propiolate (1e) was largely converted to the cyclized product 2e, and 3e was isolated as the minor product.

The ratio of 2e versus 3e did not change very much under high dilution conditions, i.e., slow addition of triphenylstannane using a syringe pump or in situ generation of triphenylstannane.

Use of tributylstannane in place of triphenylstannane resulted in generally lower over-all yield of products. For example, relatively low yield of lactones 2c-e were obtained when propiolates 1c-e reacted with tributylstannane. In these cases, Z and E isomers of 3c-e could be separated from each other, but none of the isomers were predominant.



	Substrate 1			R_3SnH	Time (hrs)[a]	Yields(%)[b]	
	R^1	R^2	R^3	R		2[c]	3(Z/E)
1a	H	H	H	Ph	4	40	d
1b	Me	H	H	Ph	4	42	45
1c	Me	Me	H	Ph	4	26	42
				Bu	6	21	14(8/6)
1d	H	$-(CH_2)_3-$		Ph	3	18	72
				Bu	2.5[e]	16[g]	10(4/6)
1e	Ph	H	H	Ph	4	62	21
				Ph[f]	4	34	41
				Bu	4	37	27(15/12)
				Ph	2.5[e]	70	30

a. Reaction conditions: 0.01-0.02 M in benzene under reflux, cat. AIBN, 1.2 equiv. of stannane. b. Isolated yields. c. In most cases, Z-isomers were isolated exclusively. A small amount of the E-isomer was also obtained from 1a. d. Difficult to isolate. e. The stannane was added by a syringe pump for 2 hours. f. Triphenylstannane was prepared in situ from triphenylstannyl chloride and sodium cyanoborohydride in t-butanol. g. Exclusive formation of the cis-fused bicyclic lactone.

α-(Triphenylstannyl)methylene-γ-butyrolactones were quite stable under the usual destannylation conditions, but α-(tributylstannyl)methylene analogues were easily transformed to α-methylene-γ-butyrolactones. For example, 2e (R=butyl) was destannylated in 75% yield when it was treated with HCl or HI in ether or benzene for 4 hours.

In conclusion, radical cyclization of allylic propiolates should present an alternative way in the synthesis of α-methylene-γ-butyrolactones, particularly in view of the ready availability of the substrate from allylic alcohols.

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