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THE CYCLIZATION REACTION OF 5-HEXENOYL CHLORIDE WITH TRI-*n*-BUTYLTIN HYDRIDE

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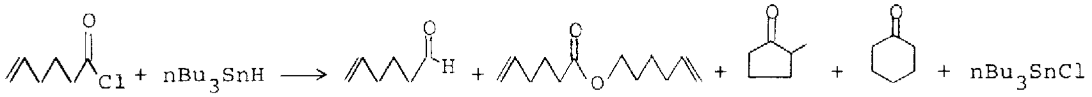
Abstract: The title reaction under various conditions of solvent, temperature and concentration was found to give 1,5 cyclization product and the typical acyclic reduction products.

Acid chlorides are reduced by organotin hydrides to give the corresponding aldehydes and esters.[1] We are studying the reaction of various alkenoyl acid halides with tri-*n*-butyltin hydride, principal of which is 5-hexenoyl chloride. Čeković[2] has reported that this reduction in boiling benzene gives cyclohexanone as the only cyclization product, and that the other competing reactions of the acyl radical which would produce 5-hexenal and 5-hexenyl-5-hexenoate occur to a very small extent.

The purpose of this paper is to report an entirely different set of results. In our hands the reduction of 5-hexenoyl chloride with tri-*n*-butyltin hydride at various temperatures, solvents and concentrations yielded 2-methyl cyclopentanone not cyclohexanone, as the major cyclization product and in all cases 5-hexenal and/or 5-hexenyl-5-hexenoate were found in significant quantities (eq. 1 and Table).



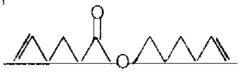
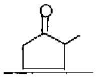
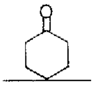
(1)

The 2-methyl cyclopentanone was isolated from several benzene (83°) reaction mixtures. Both the IR and NMR spectra of the isolated material were identical to the spectra of a commercial sample of the ketone.[3] IR (CCl_4): 2965 cm^{-1}

(C-H of $-CH_3$), 1750 cm^{-1} (C=O) and 1380 cm^{-1} ($C-CH_3$). NMR δ ($CDCl_3$): 1.07 (d, CH_3-CH-), 1.90 (m $(CH_2)_2$); 2.08 (m, $H-C-CH_2$). All other compounds were routine products for this type of reduction and they were identified by glc comparison with authentic samples which were independently synthesized.[4]

TABLE

The Reduction of 5-Hexenoyl Chloride
with Tri-n-butyltin Hydride[a]

Solvent	Temp (°C)	n-Bu_3SnH Conc. (M)	% Yield[b]		
					
Benzene	83[d]	0.40	c	33.6	6.4
	70[d]	0.50	15.6	15.7	3.0
	70[e]	0.25	10.0	20.1	4.7
	70	0.19	6.6	26.7	4.5
	40	0.50	41	7.5	≤.3
	40	0.46	39	8.0	≤.8
	40[e]	0.25	26.8	8.8	2.5
	40	0.19	23.1	13.2	1.4
Cyclohexane	83[d]	0.50	c	9.2	2.9
	70	0.24	30.9	19.6	3.2
	40	0.50	35	2.3	0.4
	40[e]	0.25	42.8	12.3	2.5
THF	83[d]	0.50	c	14	4.8

[a] Reactions were run in sealed, degassed ampoules using equimolar amounts of the hydride and acid chloride with a 3-4 mole % of AIBN. The ampoules were then submerged in a constant temperature bath.

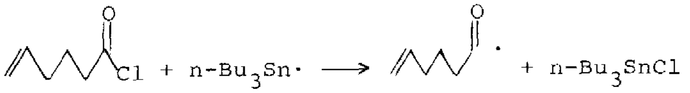
[b] The yields of the ester and both ketones were determined by glc using an internal standard. The balance of product was assumed to be 5-hexenal since there were no peaks unaccounted for in the glc. A limited exception to this involves some runs in which small amounts of what we have tentatively identified as 2-methylcyclopentyl-5-hexenoate was found. The yield of hexenal was not determined because aldehydes in the presence of the organotin chloride gave consistently low results (as determined from known mixtures with and without added organotin chloride).

[c] Not assayed.

[d] These yields are the average of 3 runs.

[e] These yields are the average of 2 runs.

The mechanism of this reduction involves the intermediacy of an acyl radical[1(a)] (eq. 2). This radical can then react with another molecule of organotin hydride to produce the aldehyde (eq. 3) or attack a molecule of aldehyde to form the radical precursor to the ester[1(b)] (eq. 4 & 5). Either course would constitute a propagation step.



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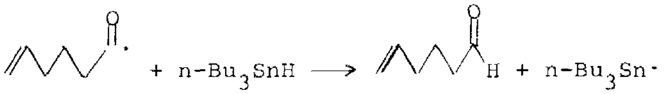

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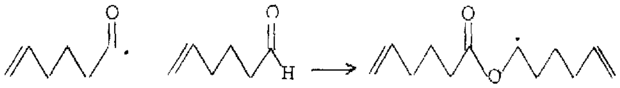

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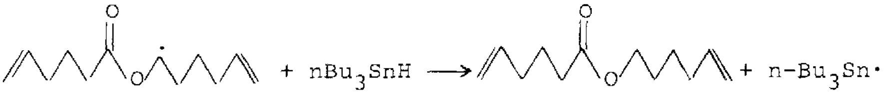


(5)

The uniqueness of this system lies in the possibility of rearrangement by intramolecular addition of the acyl radical to the carbon double bond, a well known process under conditions similar to ours and involving alkenyl radicals.[5] The addition could occur at either end of the alkene system, 1,5 or 1,6, yielding two different radicals which could react with tri-n-butyltin hydride to produce 2-methyl cyclopentanone and cyclohexanone (Figure 1).

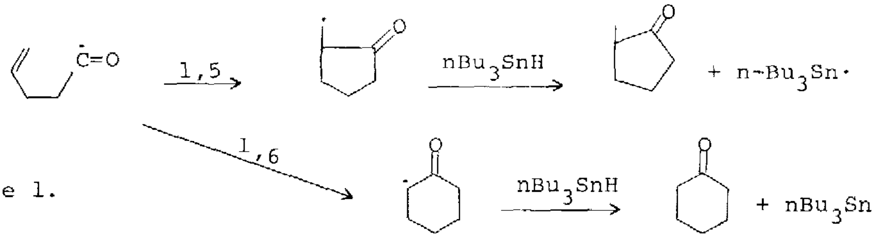
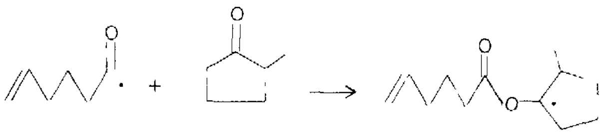


Figure 1.

The results of our study clearly show 1,5 cyclization to be the preferred mode of cyclization. Since extended reaction times produce no difference in product distribution and since the cyclohexanone product was never favored we have assumed that the cyclization is not reversible. This assumption is under investigation.

The effect of concentration and temperature follows the results reported by Walling and others[5] for the 5-hexenyl radical. That is both high temperature an dilution favor cyclization. The extent of cyclization in the 5-hexenoyl radical is less probably owing to its additional capture by 5-hexenal to eventually produce the ester or attack upon the cyclic ketone to eventually produce an ester[1(b); note (b) in Table] (eq. 6 & 7). Alternatively, the cyclic ester could be produced by cyclization of the radical which is the precursor of 5-hexenyl-5-hexenoate (eq. 8) followed by (7).



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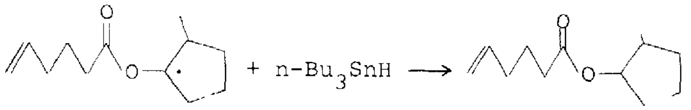

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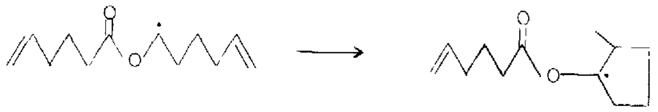

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b) E. J. Walsh, Jr. and H. G. Kuivila, *ibid.*, **88**, 576 (1966).

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