

ORGANOTIN ROUTE FOR SPECIFIC REDUCTIVE RING OPENING OF VINYL-CYCLOPROPANES

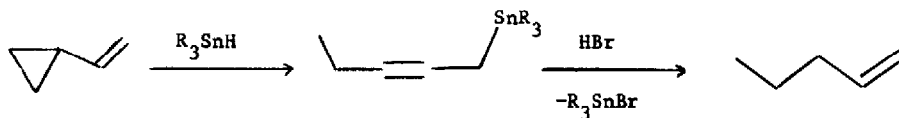
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Selective reduction of the ring in vinylcyclopropanes is difficult to realize. Diimide selectively reduces the ethylenic bond (1), as does catalytic hydrogenation to yield cyclic and acyclic saturated hydrocarbons (2). Also whilst dissolving metals readily reduce the ring, the reaction is accompanied by displacement of the double bond; thus, vinylcyclopropane is reduced to give 2-pentene isomers and only negligible quantities of 1-pentene (3).

We report here a rapid high yield method of ring hydrogenation without change in the double bond in the product. The procedure involves radical addition between the vinylcyclopropane and an organotin hydride, followed by protolysis of the resulting adduct:



The hydrostannylation of 1,1-dichloro-2-vinylcyclopropane (4), is the only example of this type of ring opening reaction in the literature, however the protolysis of allylorganostannanes is well documented and transposition of the double bond generally occurs (5).

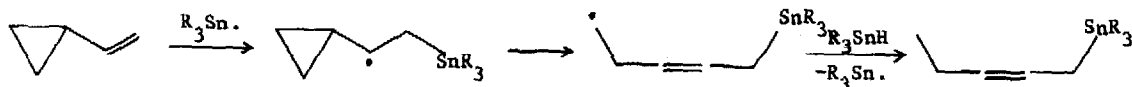
Two series of investigations were made:

a) Addition of trimethyltin hydride to the vinylcyclopropane under UV irradiation, followed by isolation of the resulting adduct and subsequent protolysis with hydrogen bromide.

b) Addition of tributyltin hydride to the vinylcyclopropane under UV irradiation, followed immediately with protolysis by titration with an ethanolic (or methanolic) solution of HBr . This technique is of greater interest as a synthetic method as a result of the easy preparation and use of tributyltin hydride. The initial addition reaction is also catalysed by azobisisobutyronitrile (AIBN).

The formation of the adduct by hydrostannylation is quantitative when the double bond is terminal, and also the protolysis is quantitative in all cases observed.

The ring opening mechanism probably involves radical attack as observed with the cyclopropylketones (6) and a likely sequence might be:



For such a mechanism, the initial addition is likely to be impeded by steric factors, as is found with the terminally-substituted-vinyl compounds.

The results of the investigations are presented in the table.

Representative examples are detailed below.

Reduction of vinylcyclopropane by Me₃SnH : Irradiation in an inert atmosphere of an equimolar mixture of Me₃SnH (6g, 0.036 mole) and vinylcyclopropane (2.5g, 0.036 mole) neat or in a solvent (hexane) in a sealed tube (utilised in this case due to the high volatility of the alkene) at ambient temperature for 1 hour, gave a quantitative yield of the adduct (absence of starting material was considered total due to the absence of characteristic absorptions (1833, 3080, 1640 cm⁻¹) in the IR spectrum).

Distillation of the adduct was carried out with a yield of 88% (b.p. 73-74°/30 mm. Analysis (C₈H₁₈Sn) calc. CZ : 41.20, HZ : 7.72 ; found CZ : 42.05, HZ : 7.72.

Chromatography on a 15% XF 1150 column at 70°C indicated a mixture of 65% trans and 35% cis isomers. The isomers were identified following separation by preparative chromatography (δ_{cis} 760 cm⁻¹ ; δ_{trans} 960 cm⁻¹).

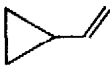

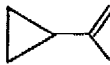
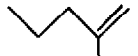
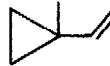
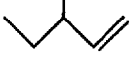
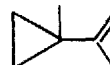
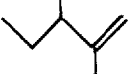
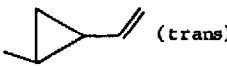


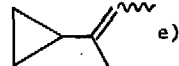
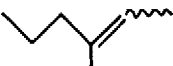
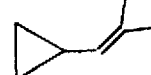

¹H-NMR (CCl₄) δ = 0.09 and 0.10 (two s, 9H), 1.00 (t, 3H), 1.70 (d, 2H), 1.7-2.4 (m, 2H), 4.8-5.7 ppm (m, 2H).

The protolysis is achieved by bubbling HBr into an ethanolic solution of the isomers of the organotin adduct (5g, 0.021 mole), whilst the extent of reaction was monitored by NMR sampling. Distillation at atmospheric pressure gave 1-pentene (yield 76%, b.p. 30-31°C) identified by comparison with an alternatively prepared sample (7).

Reduction of isopropenylcyclopropane by Bu₃SnH : Irradiation at ambient temperature for 1 hour of an equimolar mixture of Bu₃SnH (10.5 g, 0.036 mole) and isopropenylcyclopropane (3g, 0.036 mole) in a pyrex flask gave complete reaction. The adduct was cleaved subsequently without distillation. An ethanolic solution (20 ml) of HBr (1g HBr in 25 ml ethanol) was added dropwise to an ethanolic solution of the organotin adduct (4g, 0.011 mole), and a slightly exothermic reaction was observed. Scission of the tin-carbon bond gave 2-methyl-1-pentene in good yield (87%), after distillation at atmospheric pressure (b.p. 61°C). The olefin was identified by comparison of its IR, NMR spectra and chromatography with an alternatively prepared sample (8).

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Vinylcyclopropanes	Adducts b) (yield : % for R=Me)	acyclic hydrocarbons	yield % a)	
			R=Me	R=Bu
	$R_3SnCH_2CH=CHCH_2CH_3$ (88)		76	84
	$R_3SnCH_2C(CH_3)=CHCH_2CH_3$ (89)		82	87
	$R_3SnCH_2CH=C(CH_3)CH_2CH_3$ (87)		79	84
	$R_3SnCH_2C(CH_3)=C(CH_3)CH_2CH_3$ (87)		71	81
 (trans)	$R_3SnCH_2CH=CHCH_2CH_2CH_3$ } $R_3SnCH_2CH=CHCH(CH_3)_2$ } c) (84)	 }  }	78 c)	78 c)
 e)	$R_3SnCH(CH_3)C(CH_3)=CHCH_2CH_3$ d)			48
	$R_3SnC(CH_3)_2CH=CHCH_2CH_3$			0 f)

- a) All reported yields which are based on the initial quantity of the vinylcyclopropane relate to the quantities of product isolated after distillation.
- b) The organotin adducts are mixtures of the cis and trans isomers.
- c) The two products are approximately equivalent in yield ; linear : 53% ; branched : 47%
- d) Formation of the adduct was only observed following initiation with AIBN at 80°C (sealed tube) using a slight excess of Bu_3SnH .
- e) Mixture of cis and trans isomers.
- f) No reaction was observed, even with extensive UV irradiation or AIBN initiation.

TABLE - Reductive ring opening of vinylcyclopropanes

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