

Preliminary communication

Use of high pressure in the reduction of organic chlorides with tri-*n*-butyltin hydride

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Abstract

The use of the high pressure technique enables reduction of organic halides by tri-*n*-butyltin hydride to be carried out in the absence of a catalyst or free radical initiator. It leads to a better conservation of the structure of the starting material during the reduction. In the case of some unsaturated halides, a new chemoselectivity has been observed in favour of the addition of the hydride on the carbon-carbon double bond.

Organotin hydrides are very useful reagents for reduction of organic halides [1,2]. Although generally performed under free radical conditions the reactions can also be carried out in the presence of catalysts such as palladium(II) [3]. We report here the reduction of chloro compounds with tri-*n*-butyltin hydride (TBTH) under high pressure [4] in the absence of catalyst or free radical initiator.

High pressure experiments were performed in a piston-cylinder apparatus designed for pressure up to 1.5 GPa [5]. A mixture of the freshly distilled organic halide and the tin hydride in 10% excess was pressurized in a Teflon cell at the chosen temperature.

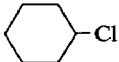

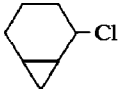

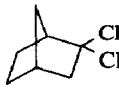
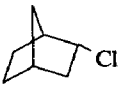
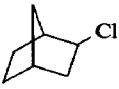
A. Reduction of saturated organic halides (Table 1)

Under high pressure, organic chlorides were reduced in the absence of free radical initiator (experiments 2, 4, 5 and 7). However, except in the case of 2,2-dichloronorbornane (experiment 7) the substitution was slower than when initiated with UV light or free radical sources. An interesting observation in experiment 5 [5,6], was that there was good retention of the cyclopropyl ring [7]. Surprisingly, in the reduction of 2,2-dichloronorbornane [8] (experiment 7), the *endo/exo* ratio [9] related to the hydrogen transfer step was not affected by the pressure.

Since 1-bromooctane reacted readily with TBTH at room temperature the re-

Table 1

Reduction of saturated organic halides with tri-n-butyltin Hydride under high pressure

Experiment	Starting material	Conditions	Products	Yield (%)			
1	$\text{CH}_3(\text{CH}_2)_7\text{Br}$	1.4 GPa, 60 °C, 24 h	$\text{CH}_3(\text{CH}_2)_6\text{CH}_3$	100 ^a			
2	$\text{CH}_3(\text{CH}_2)_7\text{Cl}$	1.4 GPa, 60 °C, 24 h	$\text{CH}_3(\text{CH}_2)_6\text{CH}_3$	41 ^a			
3	$\text{CH}_3(\text{CH}_2)_7\text{F}$	1.4 GPa, 60 °C, 24 h	$\text{CH}_3(\text{CH}_2)_6\text{CH}_3$	— ^a			
4		1.4 GPa, 60 °C, 24 h		74 ^a			
5		1 GPa, 55 °C, 48 h		10	4	86	65 ^b
6		UV, 5 °C, 4 h		94	2	4	90 ^b
7		1.2 GPa, 49 °C, 24 h		91	9	97 ^c	
8		$[\text{PhCO}_2]_2$, 80 °C, 1 h		90	10	89 ^c	

^a GC analysis by comparison with authentic samples. ^b Mass spectrometry and GC analysis. ^c ¹³C NMR analysis.

agents were mixed at 0 °C before pressurization (experiment 1). 1-Fluorooctane was not reduced under high pressure (experiment 3) but fluoro compounds are also not reduced under free radical conditions except in the case of certain specific compounds (10).



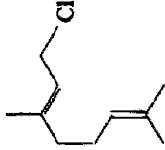
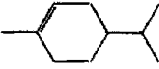
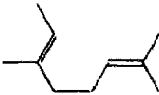
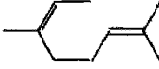

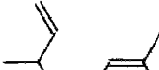
B. Reaction of unsaturated organic halides (Table 2)

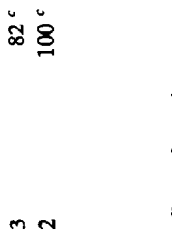



Vinyl chlorides [11] were slightly more reactive under pressure than under free radical conditions, but yields were still low (experiments 1–4), the major product being that formed by addition of the tin hydride to the dechlorinated compound.

With allylic chlorides, TBTH under pressure proved to be an efficient dechlorinating agent (experiments 8, 9 and 11). It gave a better conservation of the structure of the starting material than reactions under free radical conditions. This is probably due to the fact that the isomerization of the intermediate stabilised radical [12] is strongly retarded by the pressure. In the reduction of the neryl chloride, use of the high pressure induced a cyclization process with formation of a small amount of *para*-menthene (experiment 11).

When the chlorine atom is attached to a more remote carbon atom (experiments 13 to 15), the situation is totally different, a competition arising between substitution and addition on the double bond. Thus under free radical conditions the reaction with TBTH led selectively to dechlorination, whereas the high pressure conditions led selectively to addition to the double bond. This selectivity could be due to the fact that addition has a larger negative volume of activation than the substitution, which means that there will be a larger increase of rate with pressure in the case of the addition [13].

Table 2
Reaction of unsaturated organic halides with tri-n-butyltin hydride under high pressure

Experiment	Starting materials	Conditions	Products	Yield (%)
1	PhCH=CClMe	1.4 GPa, 60 °C, 24 h	PhCH=CHMe	16 ^a
2	Z/E 1/99	AIBN, 90 °C, 20 h	Z/E 5/26	13 ^a
3	Z/E 1/99	1.4 GPa, 55 °C, 24 h	Z/E 10/90	21 ^a
4	Z/E 95/5	AIBN, 90 °C, 20 h	Z/E 2/16	11 ^a
5	Z/E 95/5	AIBN, 90 °C, 20 h	Z/E 11/89	-
6	PhCl	1.4 GPa, 70 °C, 48 h	PhH	-
7	PhF	1.4 GPa, 60 °C, 48 h	PhH	-
8	PhCH ₂ Cl	1.3 GPa, 60 °C, 48 h	PhMe	100 ^a
9		1.3 GPa, 60 °C, 24 h		100 ^b
10		1.3 GPa, 30 °C, 24 h UV, 30 °C, 24 h	 -  96  2  2  18	70 ^c 100 ^c

11		1.3 GPa, 25 °C, 24 h UV, 30 °C, 24 h	27	5	65	3	82 ^c
12			-	49	49	2	100 ^c
			$\text{Bu}_3\text{Sn}[\text{CH}_2]_6\text{Cl}$				
13		1.4 GPa, 60 °C, 24 h	94	4		2	98 ^d
14		AIBN, 90 °C, 16 h	-	28		72	58 ^d
			$\text{Bu}_3\text{Sn}[\text{CH}_2]_4\text{CHClMe}$				
15		1.3 GPa, 50 °C, 24 h	100		-	100	39 ^d
16		AIBN, 90 °C, 16 h	-				64 ^d

^a GC analysis by comparison with authentic samples prepared separately. ^b Based on the yield of tri-n-butyltin chloride. ^c Structure established by ¹³C NMR. ^d ¹H NMR, GC and mass spectrometry analysis.

We have shown that reduction of organic chlorides with tri-*n*-butyltin hydride under high pressure does take place but rather slowly. This feature allows observation of new chemoselectivities, as demonstrated by the case of 5- and 6-chlorohexene for which the double bond undergoes hydrostannation without loss of the chlorine atom. We are seeking to extend this type of chemoselectivity to other systems that could lead to compounds containing a reactive tin-carbon bond along with another functionality.

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