Stereoselective hydrostannation of diacrylate and dimethacrylate esters of galactaric acid derivatives: cyclohydrostannation vs diaddition

V. Fabricio Terraza,[a][b] Darío C. Gerbino,[a][c] and Julio C. Podestá [a]

INQUISUR, Departamento de Química, Universidad Nacional del Sur (UNS)-CONICET, Avenida Alem 1253, 8000 Bahía Blanca, Argentina
E-mail: jpodesta@uns.edu.ar

Abstract

This paper reports a study on the free radical hydrostannation of ((4S,4'R,5R,5'S)-2,2,2',2'-tetramethyl-[4,4'-bi(1,3-dioxolane)]-5,5'-diyl)bis(diphenyl methylene) diacrylate (**1**) and dimethacrylate (**2**) with triorganotin hydrides, R_3SnH (R = Me, *n*-Bu, Ph). Preliminary investigations show that these reactions could lead to mixtures of products of cyclohydrostannation and/or mono- or diaddition according to the organotin hydrides employed and the reaction conditions used. The addition of **Me_3SnH** to **1** afforded a mixture of three organotin compounds from which it was obtained pure the new 13-membered macrodiolide **3** (48%). The other two organotins could not be separated. The addition of ***n*-Bu_3SnH** to diester **1** led to a mixture of two organotins, the one in major proportion (91%) being the product of diaddition **7**. The minor product **6a** (9%) could not be isolated pure. The hydrostannation of **1** with **Ph_3SnH** led to one organotin: the product of diaddition **8**. The hydrostannation of the dimethacrylate **2** with the organotin hydrides R_3SnH (R = Me, *n*-Bu, Ph) under the same reaction conditions, led in the three cases to mixtures containing mainly diaddition products, and no cyclization products were detected. Some physical characteristics of the new compounds including selected values of ^1H, ^{13}C, and ^{119}Sn, NMR are included.

Keywords

hydrostannation, cyclohydrostannation, unsaturated diesters of galactaric acid derivatives

Introduction

We have already reported a new method which enables the synthesis of 11-membered macrodiolides starting from TADDOL unsaturated diesters via a tandem cyclohydrostannation reaction using triorganotin hydrides and diorganotin chlorohydrides. The new macrocycles were obtained in high global yields and with very good diastereoselectivity [1]. We also studied the effect of changing the number and the steric volume of the substituents on the structure of the reaction products, i.e., macrocycles and/or diaddition products [2]. In order to determine the effect of the length of the starting unsaturated diesters on the nature of the products, we considered it of interest to study the addition of organotin hydrides to unsaturated diesters derived from D-(+)-galactose. Now, the preliminary results of these investigations are described.

Results and Discussion

Taking into account our previous results, the addition under free radical conditions of triorganotin hydrides (R_3SnH) to ((4S,4'R,5R,5'S)-2,2,2',2'-tetra methyl-[4,4'-bi(1,3-dioxolane)]-5,5'-diyl)bis(diphenyl methylene) di acrylate (**1**) and di meta acrylate (**2**) could lead to products of both cyclohydrostannation (**I**) and/or di addition (**II**), as shown in Scheme 1.

The hydrostannation of unsaturated diesters **1** and **2** with organotin hydrides R_3SnH (R = Me, n-Bu, Ph), were carried out under argon, at 75 °C, with stirring, in toluene and, in one case, without solvent, using azo-bis-isobutyronitrile (AIBN) or UV radiation as radical initiators. The reactions were followed by IR (observing the disappearance of the Sn-H absorption) and ^1H NMR spectroscopy (observing olefin disappearance and product formation). In all cases, the optimum times of reactions and hydride/olefin ratios required for a quantitative yield (with respect to olefin) were determined.

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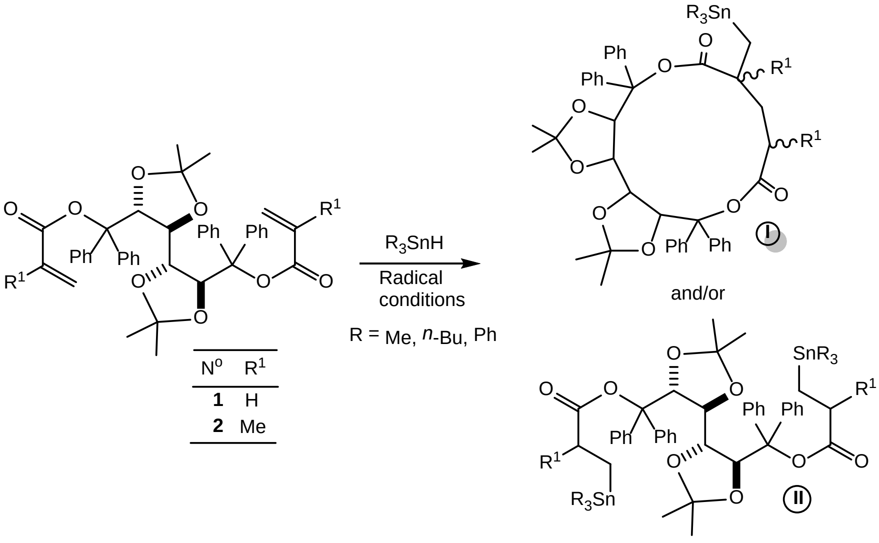
[a] Universidad Nacional del Sur (UNS), Argentina.
[b] CIC-PBA, Argentina, fabricioterraza87@hotmail.com
[c] CONICET, Ciudad de Buenos Aires, Argentina, dgerbino@uns.edu.ar

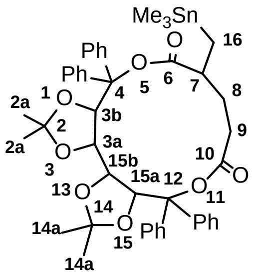
The addition of Me_3SnH in THF to diester **1**, at 75 °C, using a ratio tin hydride/**1** = 2.1 led, after 12 h, of reaction to a mixture of three organotin compounds as shown by the ^{119}Sn NMR spectroscopic analysis. Due to the fact that with this substrate the cyclohydrostannation should lead to the creation of one new stereogenic center, a maximum of two diastereomers were expected.



Scheme 1. Radical hydrostannation of unsaturated diesters **1** and **2**.

The ^{119}Sn-NMR spectrum of the mixture showed a resonance at -3.34 ppm (48%), another at 0.07 ppm (20%), and a third signal at 5.64 ppm (32%). The compound in higher proportion was separated pure by column chromatography using silica gel 60 as adsorbent. The NMR analysis together with FTIR data (see Table 1) and elemental analysis clearly showed that the major product was the macrocycle **3** (see Table 1). Thus, as seen in Table 1, the ^{13}C-NMR spectrum shows the existence of two carbonyl groups (C-6 and C-10) one of them with a ^{3}J(C,Sn) coupling constant(C-6). The presence of the two carbonyls is confirmed by the FTIR spectrum, that shows two peaks ν_{CO}: 1760 and 1732 cm^{-1}. The other two organotins present in the crude product could not be obtained pure. They probably are products of addition (type II, Scheme 1).

Table 1. Some FT-IR, ^{1}H-, ^{13}C, and ^{119}Sn-NMR spectroscopic data of compound **3**.[1]



③

	Me-Sn	C-6	C-7	C-8	C-10	C-16
^{13}C-NMR [a] (ppm)($CDCl_3$)	-8.75 (33.4)	172.99 (39.9)	53.58 (NO)	31.73 (41.0)	171.63	15.33 (341.4)
^{1}H-NMR (ppm)($CDCl_3$)	-0.08 (d, 2H); 0.00 [s, 9H, ^{2}J(Sn,H) = 52.4 Hz]; 0.68-1.06 (m, 3H); 1.19 (s, 6H); 1.28 (s, 6H); 1.87-2.35 (m, 1H); 3.25-3.50 (m, 1H); 4.75-4.94 (m, 1H); 4.99-5.39 (m,1H); 5.89 (s, 2H); 6.90-7.70 (m, 20H).					
^{119}Sn-NMR (ppm)($CDCl_3$)	-3.34					
FTIR (cm^{-1})(nujol)	1760.05; 1732.63.					

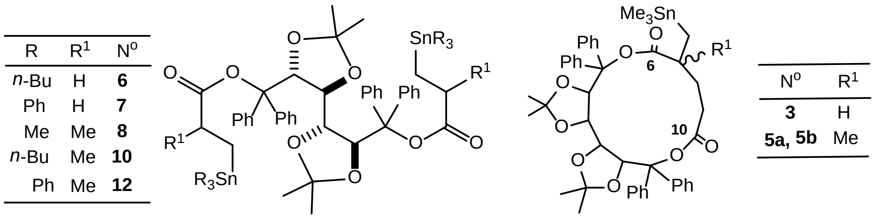
[a] [^{n}J(C,Sn)] in Hz.

On the other hand, the addition of Me_3SnH to dimethacrylate **2** led to a mixture of two organotin, the ^{119}Sn-NMR spectrum showing two signals at -0.8 and 1.5 ppm. The presence in the ^{13}C-NMR spectrum of four carbonyl signals at 164.88, 164.93, 175.29 and 175.39 ppm strongly suggest that both compounds are the macrocycles product of cyclohydrostannation. Unfortunately we were not able of obtaining these compounds pure.

We then carried out the additions of *n*-Bu_3SnH and Ph_3SnH to diacrylate **1** and dimethacrylate **2** using the same protocol. These additions followed a different pattern. The ^{119}Sn NMR spectroscopic analysis of the crude products obtained in these additions showed in all cases the formation of mixtures of various organotins. A summary of the results obtained and some other information are included in Table 2.

Hydrostannation of unsaturated diester **1** with *n*-Bu_3SnH afforded a mixture of two organotins (Table 2). The compound in higher proportion in the mixture is the product of diaddition **5** (91%), which we could not separate pure. Similarly, the addition of Ph_3SnH led just to one organotin: the product of diaddition **7**, as shown in Table 2.

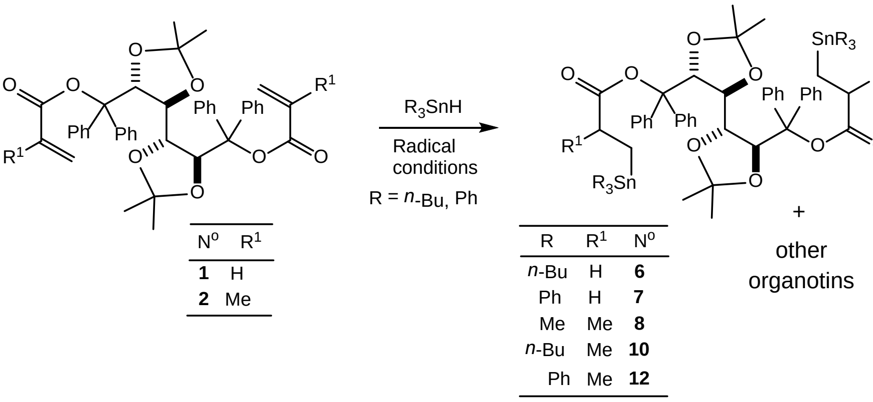
Table 2. Triorganotin hydrides additions to unsaturated diesters **1** and **2**.[a]



Reaction N°	R	Ester N°	Time (h)	Adduct N° [b]	^{119}Sn-NMR (ppm) [c]	% in the mixture	^{13}C-NMR C=O (ppm)	
							C-6	C-10
Me	Me	**1**		**3** **4a** **4b**	-3.34 -0.1 5.6	48 20 32	171.63	172.99
2	Me	**2**	16	**5a** **5b**	-0.8 1.5	73 27	164.88 164.93	175.29 175.39
3[d]	*n*-Bu	**1**	1	**6a** **7**	-8.0 -7.8	9 91	173,04 (64,5)	
4	Ph	**1**	3	**8**	-98.2	100	172.56 (77.2)	
5	*n*-Bu	**2**	1	**9** **10a** **10b**	-12.0 -9.9 -9.6	60 20 20	174.84 175.17 175.30 175.57	
6	Ph	**2**	3	**11** **12a** **12b**	-104.0 -101.0 -100.8	75 12.5 12.5	174.73 174.88 175.03	

[a] The reactions were carried out in toluene, at 75 °C, using AIBN as radical initiator except when otherwise indicated. [b] The compounds with numbers and letters could not be obtained pure. Compounds with just a number indicate that the compound is either pure or that the structure is clearly supported by spectroscopy. [c] In $CDCl_3$; chemical shifts in ppm with respect to Me_4Sn. [d] Reaction carried out without solvent.

On the other hand, the additions of *n*-Bu_3SnH and Ph_3SnH to dimethacrilate **2**, led in all cases to products of diaddition (Table 2 and Scheme 2).



Scheme 2. Radical hydrostannation of unsaturated diesters **1** and **2**.

The presence in the ^{13}C-NMR spectra of carbonyl groups around 173 ppm (none below 170 ppm) supports that these compounds are the products of diaddition.

The results obtained so far demonstrate that the products of these radical additions depend on the nature of the substituents at the tin atom of the triorganotin hydrides. In the case of the Me_3SnH, the hydride addition would favor the operation of the cyclohydrostannation tandem radical mechanism.

The authors declare no conflict of interest

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