Synthesis and Reactivity of A Novel Polar Tin Hydride

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The organostannic compounds are well known for use in organic synthesis. However, their use presents a major disadvantage because of their high toxicity and the difficulty in the separation of organostannic residues in the synthesis process. In order to overcome this problem, a polar tin hydride is synthesized, which showed a remarkable reactivity with the great advantage of being able to easily recuperate organostannic residues which will be then recycled.

Key Words: Toxicity, Organotin, Separation, Chromatography, Recycling.

INTRODUCTION

The organotin compounds present an interesting reactivity[1] in organic synthesis. Indeed, they make it possible to carry out with good yields chemo, regio and stereoselectives reactions. The hydride triorganotin remains the best reagent to carry out selective reduction reactions[2-5], also to form carbon-carbon bonds by free radical route. This is due to the Sn-H weak bond and the force of the bond Sn-X thus formed.

However, the organotin compounds present a major disadvantage, related to their toxicity and their impact on the environmental[6-8]. In organic synthesis, they are difficult to separate from the final reactions products because of their high boiling point, limiting their purification by distillation and because of their low polarity making them soluble in the majority of organic solvents (difficulties of separating them by water/organic solvents). Moreover the fragility of some organotin derivatives with respect to silica limits their purifications by chromatography.

Thus, several specific methods of purification were developed to solve this problem. In this work and after analysis of the disadvantages presented by each one of these methods[10-16], we propose the synthesis of new tin hydride in which the tin atom is substituted by two polar groups, to increase the polarity of the organotin residues and will thus facilitate the separation of the desired products of the organotin residues. These latter, being able to be then recovered and recycled for further application.

EXPERIMENTAL

^{1}H NMR and ^{13}C NMR spectra were obtained with Brucker-AM200 spectrometer. The chemical shifts are expressed in ppm downfield from TMS in δ units.

The mass spectra were recorded on Jeol-JMS-DX300 spectrometer. IR spectra were measured with Shimadzu FTIR 8400 spectrometer. Shimadzu 17A gas chromatograph was used to analyze reactions. Silica gel 60 Merck 230-400 Mesh (0.04-0.063 mm) was used for column chromatography. Silica gel 60 (Merck F254) was used for TLC.

Diphenylstannate (2): A 22 g (0.064 mol) of diphenyltin dichloride in dry Et_2O (60 mL) was slowly added to a stirred and cooled (0 °C) suspension of $LiAlH_4$ (4 g, 0.1 mol) in dry Et_2O (100 mL) (Ar atmosphere). Stirring was continued for 0.5 h at 0 °C. The mixture was then quenched by slow addition of ice-water and extracted with Et_2O (3 × 50 mL). The extract was dried ($MgSO_4$) and evaporated at 35 °C. 17 g of diphenylstannate were recovered which is used crude in the following reaction.

Di(ethylene glycol)methyl allyl ether (3): To a boiling solution of potassium hydroxide (56 g, 1 mol) in THF (500 mL) and (60 g, 0.5 mol) of di(ethylene glycol)methyl allyl ether, a solution of allyl bromide (91 g, 0.75 mol) was slowly added within 1.5 h after another 3 h under reflux, the mixture is concentrated then treated with a saturated aq. NH_4Cl (40 mL) and Et_2O (70 mL). The aqueous phase is extracted with Et_2O, dried $MgSO_4$; the combined ether phase is washed with saturated aq. NH_4Cl, dried $MgSO_4$ and concentrated. Pure di(ethylene glycol)methyl ether allyl (59 g, 90 %) is distilled at 100 °C/25 mm Hg in Kugelrohr.
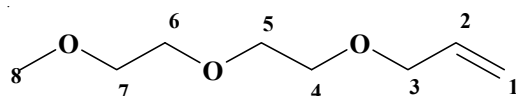

^{1}H NMR (CDCl$_3$, δ ppm): 3.4-3.5 (m, 8H, C^{4}H$_2$, C^{5}H$_2$, C^{6}H$_2$ and C^{7}H$_2$); 3.4-3.9 (m, 2H, C^{3}H$_2$); 4.9-6.1 (m, 3H, C^{1}H$_2$C^{2}H).

Diphenyl *bis*[4,7,10-trioxaundecyl]stannate (4): 15 g (0.054 mol) of diphenylstananne (2), 17.28 g (0.108 mol) of di(ethylene glycol)methyl allyl ether (3) and 200 mg of AIBN are mixed and heated gradually up to 80 °C. After 12 h of heating at this temperature we added 200 more of AIBN, then the reactional mixture is heated another 12 h. After purification chromatography (silica gel, petroleum ether/ether: 20/80) pure diphenyl *bis*[4,7,10-trioxaundecyl]stannate is obtained with 55 % yield.
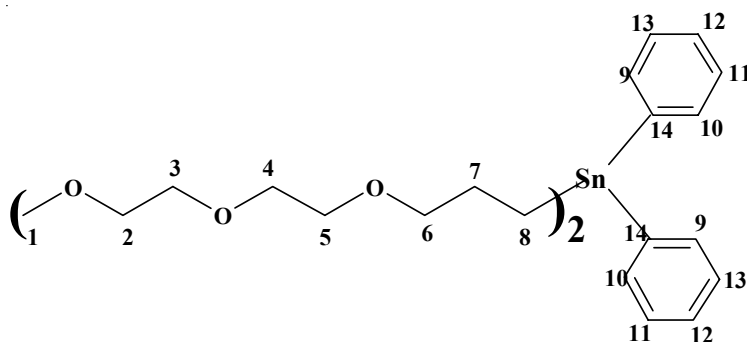
^{1}H NMR (C$_6$D$_6$, δ ppm): 1.25-1.35 (m, 4H, C^{8}H$_2$); 1.87-2.06 (m, 4H, C^{7}H$_2$); 3.35 (S, 6H, C^{1}H$_3$); 3.38-3.60 (m, 20H, C^{2}H$_2$ C^{3}H$_2$, C^{4}H$_2$ C^{5}H$_2$, C^{6}H$_2$); 7.10-7.20 (m, 6H C^{11}H, C^{12}H, C^{13}H); 7.30-7.40 (m, 4H, C^9, C^{10}). ^{13}C NMR (C$_6$D$_6$, δ ppm): 6,865 (C^8); 26,912 (C^7); 58,438 (C^1); 70,325; 70,604; 70,682; 72,096; (C^2, C^3, C^4 and C^5); 73,955 (C^6); 128,335 (C^{11}, C^{12}, C^{13}); 136,938 (C^9, C^{10}); 140,831 (C^{14}).

Phenyl *bis*[4,7,10-trioxaundécyl]bromostannate (5): At -50 °C Br$_2$ (2.56 g, 0.016 mol) in methanol (70 mL) is slowly added to a solution of diphenyl *bis*[4,7,10-trioxaundecyl]stannate (4) in methanol (200 mL). At the end of the addition, the mixture is left to return at an ambient temperature and under agitation for 12 h. After purification by chromatography (silica gel, ethyl acetate) pure phenyl *bis*[4,7,10-trioxaundecyl]bromostannate is obtained with 83 % yield.
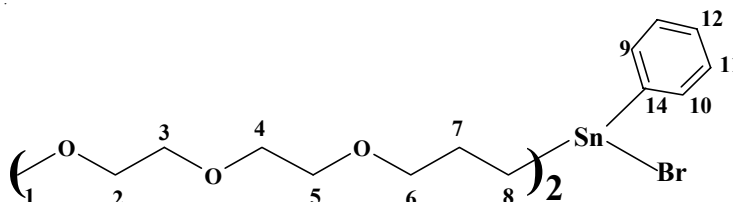
^{1}H NMR (C$_6$D$_6$, δ ppm): 0.68-0.80 (m, 4H, C^{8}H$_2$); 1.00-1.16 (m, 4H, C^{7}H$_2$); 2.28 (S, 6H, C^{1}H$_3$); 2.40-2.56 (m, 20H, C^{2}H$_2$ C^{3}H$_2$, C^{4}H$_2$ C^{5}H$_2$, C^{6}H$_2$); 6.24-6.44 (m, 3H C^{11}H, C^{12}H, C^{13}H); 6.88-7.00 (m, 2H C^{9}H, C^{10}H). ^{13}C NMR (C$_6$D$_6$, δ ppm): 15,916 (C^8); 26,250 (C^7); 58,418 (C^1); 70,212; 70,309; 70,385; 72,003 (C^2,C^3, C^4 and C^5); 72,752 (C^6) 128,355 (C^{11}, C^{12}, C^{13}); 136,147 (C^9, C^{10}); 142,930 (C^{14}).

Phenyl *bis*[4,7,10-trioxaundécyl]stannate (6): 22 g (0.064 mol) of bromstannate (5) in dry Et$_2$O (80 mL) was slowly added to a stirred suspension of LiAlH$_4$ (1 g, 0.026 mol) in dry Et$_2$O (100 mL) (Ar atmosphere). Stirring was continued for 2 h at reflux. The mixture was then quenched by slow addition of ice-water and extracted with Et$_2$O (3 × 50 mL). The extract was dried (MgSO$_4$), concentrated and chromatographed (silica gel ether = giving the phenyl *bis*[4,7,10-trioxaundecyl]-stannate (6): yield: (60 %).
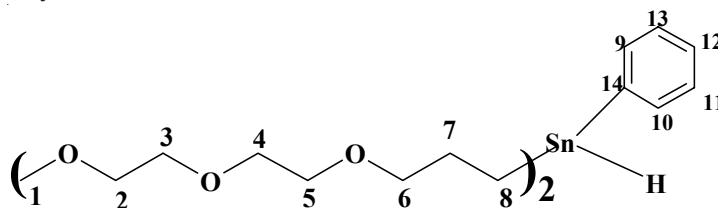
^{1}H NMR (C$_6$D$_6$, δ ppm): 0.76-0.91 (m, 4H, C^{8}H$_2$); 1.36-1.66 (m, 4H, C^{7}H$_2$) 2.81 (s, 6H, C^{1}H$_3$); 2.88-3.23 (m, 20H, C^{2}H$_2$, C^{3}H$_2$, C^{4}H$_2$, C^{5}H$_2$, C^{6}H$_2$); 5.39 (m, 1H, SnH); 6.76-6.91 (m, C^{11}H, C^{12}H, C^{13}H); 7.10-7.22 (m, 2H, C^{9}H, C^{10}H). ^{13}C NMR (C$_6$D$_6$, δ ppm): 6,109 (C^8); 27,172 (C^7); 58,439 (C^1); 70,311; 70,613, 70,719; 72,104 (C^2, C^3, C^4 and C^5); 73,814 (C^6); 128,254 (C^{11}, C^{12}, C^{13}); 137,118; (C^{14}, C^9, C^{10}); 140, 390 (C^{14}).

Reduction of hexadecyl halides: To 0.25 mmol halide of hexadecyl in dry toluene (5 mL). Phenyl(*bis*)-[4,7,10-trioxaundecyl]stannate (6) and 32 mg of azo(*bis*)isobutyronitrile are slowly added. Then the mixture to the reflux during various times were carried out. After evaporation of the solvent, purification by chromatography, hexadecane is identified by gas chromatography by using the reference (commercial product).

**Reduction of 1-chlorohexadecane 7A:** The hexadecane is obtained after 18 h of heating with 93 % yield.

Reduction of 1-bromohexadecane 7 B: The hexadecane is obtained after 2 h of heating with 90 % yield.

Reduction of 1-iodohexadecane 7 C: The hexadecane is obtained after 1 h of heating with 95 % yield.

Reduction of ethyl chloromalonate 7D: 1 g (1.92 mmol) of phenyl *bis*[4,7,10-trioxaundecyl]stannate, 320 mg of azo-*bis*-isobutyronitril was slowly added to a stirred solution of ethyl chloromalonate (203 mg, 1.28 mmol) in dry toluene (10 mL). Stirring was continued for 12 h at reflux. The mixture was concentrated and chromatographed (silica gel petroleum ether/ether: 80/20) giving the ethyl malonate yield: 99 %.

Reducing addition of halides on alkenes: At 80 °C during 2 h the phenyl *bis*[4,7,10-trioxaundecyl]stannate (6) in dry toluene was added to halogenous derivative and AIBN under inert atmosphere (Argon). The mixture was then left under agitation at 80 °C during 1 h, concentrated and chromatogaphed (silica gel).

Ethyl cyclohexylpropionate 10A: 460 mg (2.19 mmol) of iodocyclohaxane, 1.09 g (10.9 mmol) of ethyl acrylate in dry toluene (10 mL), 1 g (1.92 mmol) of phenyl *bis*[4,7,10-trioxaundecyl]stannate. The product was purified on silca gel column (petroleum ether/ether: 90/10), the ethyl cyclohexylpropionate was obtained with 40 % yield.
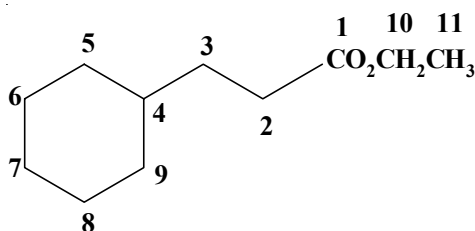
^{1}H NMR (CDCl$_3$, δ ppm): 0.75-2.12 (m, 13H, H du cycle and C^{3}H$_2$); 2.25 (t, 2H, C^{2}H$_2$); 4.0-4.15 (q, 2H, C^{10}H$_2$).

Ethyl-4,7,10-trioxaundecyl malonate 10B: 240 mg (1.25 mmol) of ethyl chloromalonate, 980 mg (6.12 mmol) of allyl ether in dry toluene (10 mL), 720 mg (1.38 mmol) of phenyl *bis*[4,7,10-trioxaundecyl]stannate (6), 200 mg of AIBN, the pure product was obtained with 38 % yield.
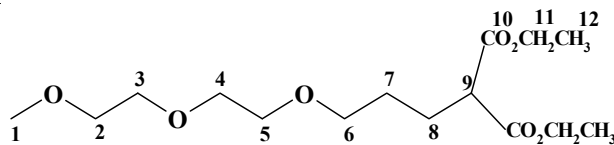
^{1}H NMR (CDCl$_3$, δ ppm): 1.30 (t, 6H, C^{12}H$_3^1$); 1.5-1.65 (m, 2H, C^{7}H$_2$); 1.85-2.05 (m, 2H, C^{8}H$_2$); 3.38 (t, 1H, C^{9}H); 3.39 (s, 3H, C^{1}H$_3$); 3.45-3.75 (m, 10H, C^{2}H$_2$, C^{3}H$_2$, C^{4}H$_2$, C^{5}H$_2$, C^{6}H$_2$); 4.18 (q, 2H, C^{11}H$_2$).

RESULTS AND DISCUSSION

Preparation of the polar tin hydride: The preparation of the polar tin hydride was carried out in three essential stages, in which the first consists in the hydrostannation of ether of allyl and methyl of the diethylene glycol (3) by diphenylstannate (2) under radical conditions to form the diphenyl *bis*[4,7,10-trioxaundecyl]stannate (4) , the latter is obtained with 55 % yield after purification on column silica gel.

The second stage consists in substituting a phenyl group of the diphenyl *bis*[4,7,10-trioxaundecyl]stannate by a bromine atom. This reaction is difficult to realize under normal conditions, the initial product can undergo a second substitution of the bond Sn-C (Sn-pH or Sn-QP) because of the aggressiveness of bromine. So and in order to avoid the second substitution we carried out this reaction at very low temperature (-50 ºC) with a very slow addition of bromine. The phenyl *bis*[4,7,10-trioxaundecyl]bromostannate (**5**) is obtained pure with 80 % yield.

Phenyl *bis*-[4,7,10-trioxaundecyl]stannate (**6**) is then synthesized by reduction of the phenyl *bis*[4,7,10-trioxaundecyl]bromostannate (**5**) by the aluminum lithium hydride, the product is obtained pure in the form of oil with 60 % yield after purification on column silica gel.
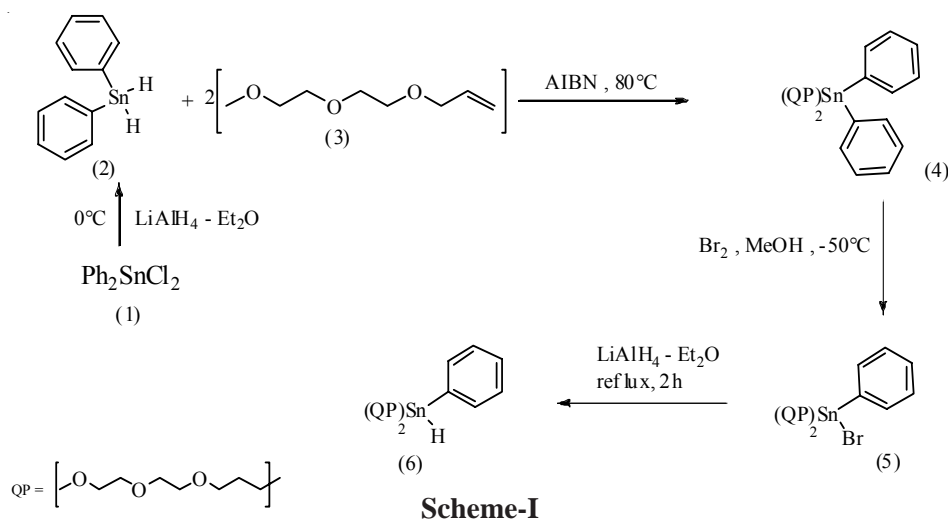
Scheme-I

Reactivity of the polar tin hydride: Initially, the reactivity of the hydride synthesized was compared with that of the hydride of tributyltin. For that, the reduction of halides of hexadecyl was studied according to the **Scheme-II**:
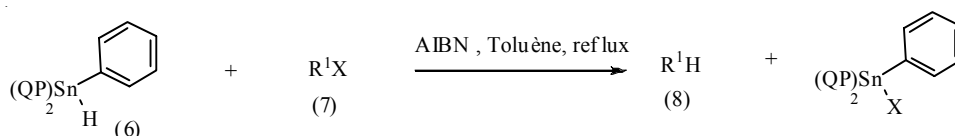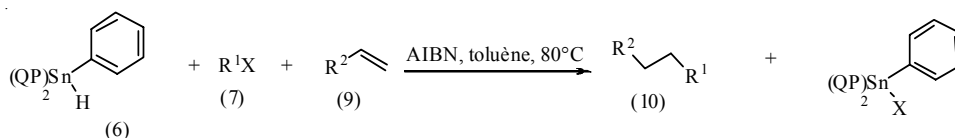

Scheme-II

The iodide and bromide derivatives are completely consumed after respectively 1 and 2 h of heating, by using a light excess of tin hydride (1.2 moles/mole of halogenous derivative).

In the case of the chloride derivative, the latter reacts completely after a heating of 18 h by using an excess of tin hydride (2 moles/mole of chlorinated derivative). For each reaction the crude product is purified on column of silica and hexadecane is recovered by elution with pure petroleum ether.

The excellent behaviour of this new hydride with respect to alkyl halides, it is explored that other potential applications for this compound by studying its reactivity in the reduction of appreciable product of polarity such as the ethyl chloromalonate, also in the reactions of reductive alkylation halogenous derivatives on alkenes[17].

Scheme-III

The results obtained are represented in Table-1.

TABLE-1
REACTIVITY OF THE POLAR TIN HYDRIDE IN THE REDUCTION OF HALIDES

Polar tin hydride	R^1X	Product	Yield (%)
6	7A: $R^1 = -C_{16}H_{33}$, X = Cl	8A: $R^1 = -C_{16}H_{33}$	93
6	7B: $R^1 = -C_{16}H_{33}$, X = Br	8A: $R^1 = -C_{16}H_{33}$	90
6	7C: $R^1 = -C_{16}H_{33}$, X = I	8A: $R^1 = -C_{16}H_{33}$	95
6	7D: $R^1 = -CH(CO_2Et)_2$, X = Cl	8B: $R^1 = -CH(CO_2Et)_2$	99

Poor yield obtained, with 80 °C, is probably due to a polymerization of the acrylic derivatives[18]. In order to avoid these reactions we carried out the radical reactions at ambient temperature witch BEt_3/O_2 as a radical initiator. The results obtained are represented in Table-2.

TABLE-2
REACTIVITY OF THE POLAR TIN HYDRIDE IN THE REACTIONS OF
REDUCTIVE ALKYLATION HALIDES

Polar tin hydride	Alkene	Product	Yield (%)	
			AIBN/80°C	Et$_3$B/O$_2$ rt
6	7E: R^1= -C$_6$H$_{11}$, 9A: R^2 = -CO$_2$Et	10A: R^1 = -C$_6$H$_{11}$, R^2 = -CO$_2$Et	40	65
6	7D: R^1 = -CH(CO$_2$Et)$_2$, 9B: R^2=CH$_2$(CH$_2$CH$_2$O)$_2$OCH$_3$	10B: R^1 = -CH(CO$_2$Et)$_2$, R^2 = -CH$_2$(CH$_2$CH$_2$O)$_2$OCH$_3$	38	63

Conclusion

As a result of the increasing interest of the organotin reagents in organic synthesis, in this work, the synthesis of a new tin hydride containing two polar groups is developed. This intermediary showed a remarkable reactivity in the free radical reactions, the reactional mixtures elected on silica column show an excellent separation of the desired products of under organic tin derivatives. The latter are recovered and recycled with a rate of 90 % for a new re-use, thus avoiding the contaminations of the desired products of reaction.

REFERENCES

1. S.D. Scilliano, J.J. Gimida and J.V. Headley, *Environ. Toxicol. Chem.*, **16**, 521 (1997).
2. C.G. Cho and Y.W. Kim, *Tetrahedron Lett.*, **42**, 8193 (2001).
3. R. Alibés, P.D. March, M. Figueredo, J. Font, M. Racamande, A. Rustuellet, A.A. Tarena, J.F. Piniella and I. Parella, *Tetrahedron Lett.*, **44**, 69 (2003).
4. D.H. Kergosien and C.D. Rice, *Arch. Environ. Contam. Toxical.*, **34**, 223 (1998).
5. O.K. Halloran, J.T. Ahokas and P.F.A. Wright, *Aquatic Toxicol.*, **40**, 141 (1998).
6. D. Jargot, F. Pilliére, J.C. Protois, M. Reynier and P. Serre, Fiche Toxicologique N° 173, INRS (1997).
7. F. Ferkous, M. Degueil-Castaing, H. Deleuze and B. Maillard, *Main Group Metal Chem.*, **20**, 75 (1997).
8. F. Ferkous, D. Messadi, B. De Jeos, M. Degueil-Castaing and B. Maillard, *J. Organomet. Chem.*, **421**, 315 (1991).
9. J. Andrew and E.J. Tomas, *J. Chem. Soc. Perkin Tans. I*, 1521 (1989).
10. B. M-Matute, E. Bunuel, M. Mendez, C. N-Oberhuber, D.J. Cardenas and A.M. Echawarren, *J. Organomet. Chem.*, **687**, 410 (2003).
11. D.P. Curran and C.T. Chong, *J. Org. Chem.*, **54**, 3140 (1989).
12. H. Schumann and B. Pachaly, *Angew. Chem. Int. Ed. Engle*, **20**, 1043 (1981).
13. G. Ruel, N.K. The, G. Dumartin, B. Delmond and M. Pereyre, *J. Organomet. Chem.*, **444**, C18 (1993).
14. D.L.J. Clive and W. Yong, *J. Org. Chem.*, **60**, 2607 (1995).
15. D.P. Curran and S. Hadida, *J. Am. Chem. Soc.*, **118**, 2531 (1996).
16. R.E. Maleczka and I. Terstiege, *J. Org. Chem.*, **63**, 9622 (1998).
17. B. Giese, H. Horler and M. Leising, *Chem. Ber.*, **119**, 444 (1986).
18. B. Giese, *Angew. Chem. Int. Ed. Engl.*, **22**, 753 (1983).