Journal of Organometallic Chemistry, 232 (1982) C29—C32
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

ORGANOMETALLIC CHEMISTRY UNDER HIGH PRESSURE: TRIALKYLTIN HYDRIDE ADDITION TO UNSATURATED SYSTEMS

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(Received February 5th, 1982)

Summary

The influence of high pressure (10—14 kbars) on the reaction of tin hydrides with alkenes and ketones has been investigated and a marked increase of yields generally was observed. For cyclopropyl- and cyclobutyl-alkenes, adducts were formed with retention of the rings. The stereochemical outcomes of the reactions were modified.

Many additions of organotin hydrides have been studied under classical conditions and the value of these reducing reagents is self-evident [1]. However, the use of high pressure, although well established [2], has not yet been widely explored, especially in the field of organometallic chemistry. New extensions of known reactions as well as previously unsuccessful reactions of possible synthetic interest remain to be explored under high pressure conditions. This paper reports preliminary results obtained for tributyl- or trimethyl-tin hydride (or deuteride) additions to various alkenes and ketones.

High pressure experiments were performed in a piston-cylinder high pressure apparatus designed for pressures up to 15 kbars [3]. The working volume of the teflon cell was about 1.5 ml. The internal temperature could be adjusted from −15 to +60°C using external cooling or heating jacket.

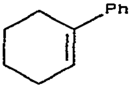
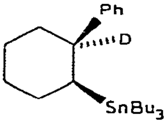
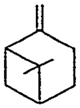
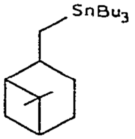
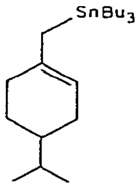
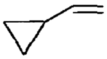
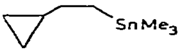
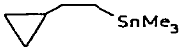
A. Hydrostannation of carbon—carbon double bonds

A mixture of freshly distilled alkene and the tin hydride (or deuteride) in 10% excess was pressurized at the desired temperature without any radical initiator. Three reactions were investigated (Table 1).

When deuterostannation of phenylcyclohexene was performed at ordinary pressure in the presence of a free radical initiator (AIBN, UV light) yields

TABLE 1

HYDROSTANNATION AND DEUTEROSTANNATION OF ALKENES

Experiment	Starting material	Organotin hydride or deuteride	Conditions	Products	Yield (%)
1		Bu_3SnD	10 kbars, 50°C 64 h, neat	 (a)	90
2		Bu_3SnH	14 kbars, 55°C 24 h, neat	 97 % (a,b)  3 % (a,b,c)	95
3		Me_3SnH	14 kbars, 55°C 24 h, neat	 61 % (b,c) $EtCH=CHCH_2SnMe_3$ E 19 % Z 20 % (b,c)	95
			14 kbars, 4°C 24 h, neat	 76.5 % (b,c) $EtCH=CHCH_2SnMe_3$ E 11.5 % Z 12 % (b,c)	70

[a] Structure established by NMR. [b] Gas chromatography and mass spectrometry analysis. [c] Compared with authentic samples prepared separately.

were less than 10%. On heating phenylcyclohexene with tributyltin deuteride at 180°C in the absence of an initior for 64 h only a 30% yield was obtained. The effect of the high pressure (exp. 1) was to increase this yield up to 90%. The regioselectivity of the addition was established by ^{13}C NMR and the stereochemistry (anti-addition only) by ^{119}Sn NMR spectroscopy [4].

The hydrostannation of β-pinene was previously studied by Shiihara et al., who obtained only the ring-opened adduct whatever the conditions used [5]. Under high pressure (exp. 2) the bicyclic structure was retained.

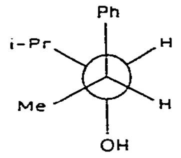
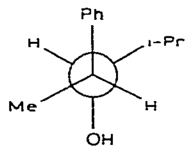
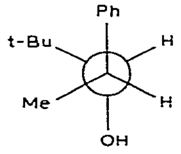
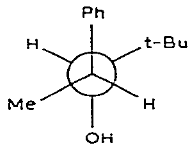
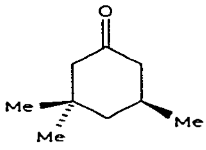
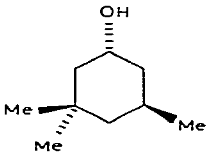
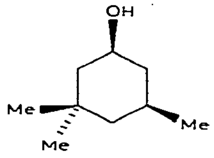
In the case of vinylcyclopropane, hydrostannation with trimethyltin hydride under atmospheric pressure and at 55 or 4°C gave low yields of adducts with only a few percent (5 to 10%) of cyclopropyl derivatives. The free radical initiated hydrostannation gave exclusively the ring-opened products in a ratio E/Z 65/35 with a yield of 88% [6]. In experiment 3, high pressure led to high degree of retention of the cyclic structure. Moreover, by using a lower temperature along with high pressure, we were able to increase the ratio between cyclic and ring-opened products.

B. Reduction of ketones

Mixtures of ketones and tributyltin hydrides (stoichiometric amounts) in methanol were pressurized under similar conditions. The intermediate alkoxytin adducts gave the corresponding alcohols directly by methanolysis [7,8]. The results are shown in Table 2.

TABLE 2

REDUCTION OF KETONES BY TRIBUTYLTIN HYDRIDE

Experiment	Starting material	Conditions	Products	Yield (%)
4	i-PrC(=O)-i-Pr	10 kbars MeOH, 55°C 24 h	i-PrCH(OH)-i-Pr (*a*)	62
5	PhCH(Me)C(=O)-i-Pr	10 kbars MeOH, 55°C 24 h	 70%  30% (*a,b*)	63
6	PhCH(Me)C(=O)-t-Bu	10 kbars MeOH, 55°C 24 h	 88%  12% (*a,b*)	57
7	 	10 kbars MeOH, 55°C 24 h	 80%  20% (*a,b*)	64

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[a] GC analysis by comparison with authentic samples prepared separately. [b] Racemic.

Under thermal conditions (MeOH, 55°C, 24 h, atmospheric pressure) the yields were respectively 4, 2 and 35% for experiments similar to 4, 5 and 7, and no product was detectable for an experiment similar to 6. These poor yields were probably due to steric hindrance, which can be overcome under high pressure: at 10 kbars yields were around 60% for experiments 4—7.

For experiment 5, no change was observed in the diastereoisomeric ratios for reactions under atmospheric or high pressure. However, in the case of experiment 7, the yield increased from 35 to 64% and the *cis/trans* ratio was changed from 9/91 to 20/80. These results are in agreement with the usual effect of pressure on sterically-hindered reactions [9].

In summary, high pressure conditions in hydrostannation reactions open new possibilities in terms of both yields (the increase of rate especially striking in the case of sterically-hindered reactions) and the course of reaction (conservations of cycles in cases where classical conditions would lead to ring opened products). Further experiments in this field are in progress.

Acknowledgements. We thank Schering France for generous gifts of chemicals.

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