Journal of Organometallic Chemistry, 127 (1977) C75—C77

Preliminary communication

SYNTHESIS AND OPTICAL STABILITY OF CHIRAL TRIORGANOTIN HYDRIDES

MARCEL GIELEN

Vrije Universiteit Brussel, TW-AOSC, Pleinlaan 2, B-1050 Brussels (Belgium)

and YVES TONDEUR

Université Libre de Bruxelles, Collectif de Chimie Organique Physique, Pleinlaan 2, B-1050 Brussels (Belgium)

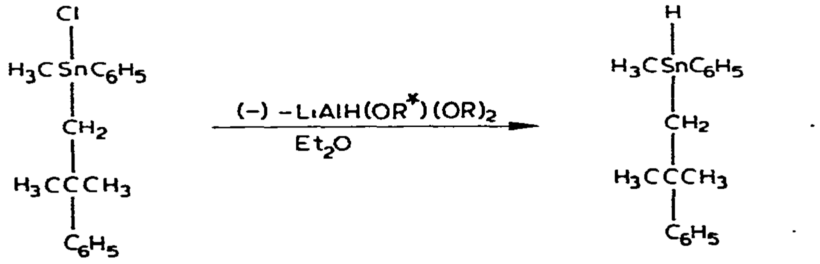
(Received January 4th, 1977)

Summary

The first optically-active triorganotin hydrides are reported, viz.: (+)- and (—)-methylneophylphenyltin hydride and (—)-t-butylneophylphenyltin hydride; they are fairly optically stable.

Several types of organotin compounds are configurationally stable on the NMR time scale: tetraorganotins [1], triorganotin hydrides [2], amines, phosphines, arsines [3], triorganostannyl-germanium [2], -molybdenum [2] and -iron compounds [4], but only tetraorganotin compounds have been isolated in optically active form [5,7]. We now report the synthesis of the first optically active triorganotin hydrides.

(+)-Methylneophylphenyltin hydride, (+)-I, has been prepared by asymmetric reduction of the corresponding racemic chloride with one of the



(±)

racemic mixture

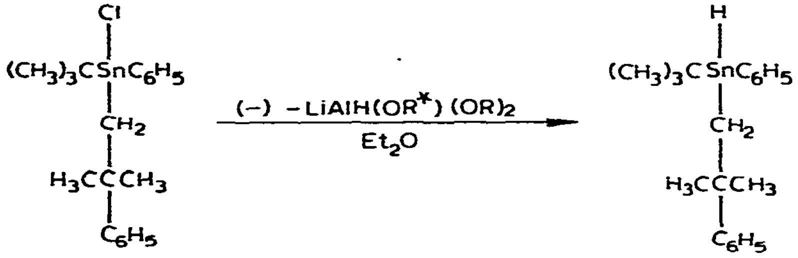
((+)–I)

optical purity unknown

chiral reducing agents described by Vigneron and Jacquet [6], viz. (—)-$LiAlH(OR^*)(OR)_2$ with R^*OH = *N*-methylephedrine and ROH = 3,5-dimethylphenol.

Compounds,(+)-I was obtained in 55% yield and has an NMR spectrum, a mass spectrum and an IR spectrum idential to those of an authentic racemic sample. The ORD-spectrum (c 5.57 in benzene) is: λ(nm), [α]*: 589, +1.80°; 578, +1.85°; 546, +2.11°; 436: +3.76°; 365, +6.13°. During 30 days at −2°C, the optical activity of the neat product decreases by only 10%. In benzene solution, there is about 50% of racemization in 17 days at room temperature. At 80°C, the optical activity of this benzene solution decreases by about 20% during 270 minutes. This corresponds to E_{act} ∿13 kcal/mole and $\log_{10}$ PZ ∿ 6.64.

(—)-t-Butylneophylphenyltin hydride (II) has been synthesized by the same method in 65% yield:



(±)

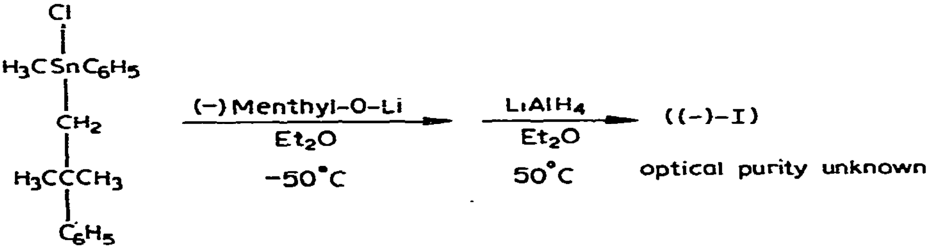
racemic mixture

((−)-II)

optical purity unknown

The ORD-spectrum of II is: λ(nm), [α]*: 589, −1.19°; 578, −1.22°; 546, −1.39°; 436, −2.38°; 365, −3.74° (c 6.45; C_6H_6).

(—)-I has also been synthesized by a method analogous** to that used by Taddei for the synthesis of optically active tetraorganotin compounds [7]:



---

[*] ± 0.05°, *t* = 30°C, in all cases.

[**] If the synthesis of the menthoxytin compound and its reduction by $LiAlH_4$ or by RMgX are carried out at lower temperatures, the optical yields are improved. For instance, methylneophyltrityltin bromide is converted by Taddei's method [7] into methylneophylisopropyltrityltin having $[\alpha]_D$ 0.00° if the synthesis is carried out at 0°C; $[\alpha]_D$ is equal to +5.1° if the synthesis is carried out at −15°C.

There is a 55% yield of (—)-I, $[\alpha]_D$ —0.51° (*c* 7.89 in C_6H_6). It is thus possible to synthesize both (+)- and (—)-methylneophylphenyltin hydride, and this will be useful for the study of stereoselective substitutions at the tin atom of this triorganotin hydride.

This second method has also been used to make optically active (—)-II ($[\alpha]_D$—0.56°, *c* 6.95 in C_6H_6; product yield: 70%; optical yield unknown).

We are now studying the stereochemistry of reactions of these optically-active and optically-stable triorganotin hydrides.

References

1 See for instance M. Gielen, C. Hoogzand, S. Simon, Y. Tondeur, I. van den Eynde and M. van de Steen, in J.J. Zuckerman (Ed.), Organotin Compounds: new chemistry and applications, Advances in Chemistry Series, 157 (1976) 249.

2 M. Gielen, S. Simon, Y. Tondeur, M. van de Steen and C. Hoogzand, Bull. Soc. Chim. Belges, 83 (1974) 337.

3 M. Gielen and Y. Tondeur, Bull. Soc. Chim. Belges, 84 (1975) 933.

4 M. Gielen, C. Hoogzand and I. van den Eynde, Bull. Soc. Chim. Belges, 84 (1975) 939.

5 M. Mokhtar-Jamai and M. Gielen, Bull. Soc. Chim. France, 9B (1972) 32; Ann. N.Y. Acad. Sci., 239 (1974) 208; Bull. Soc. Chim. Belges, 84 (1975) 197; M. Lequan and F. Meganem, J. Organometal. Chem., 94 (1975) C1.

6 J.P. Vigneron and I. Jacquet, Tetrahedron, 32 (1976) 939.

7 U. Folli, D. Iarossi and F. Taddei, J. Chem. Soc. Perkin II, (1973) 6[illegible].