*Journal of Organometallic Chemistry*, 128 (1977) 359—360


# SYNTHESIS OF AN OPTICALLY ACTIVE INDENYL ORGANOTIN COMPOUND

A.N. KASHIN *, V.A. KHUTORYANSKII, V.N. BAKUNIN, I.P. BELETSKAYA and O.A. REUTOV

*Moscow State University, Moscow (U.S.S.R.)*

(Received September 9th, 1976)

## Summary

Synthesis of optically active (+)-(3-methylindenyl)trimethyltin by interaction of (*S*)-(+)-1-methylindene with $Et_2NSnMe_3$ is described.

Several optically active organotin compounds with a metal atom bonded to a chiral center have been described [1,2], including diastereomers [3]. Organotin compounds with the tin atom as a chiral center have also been obtained [4].

We have shown that interaction of (*S*)-(+)-1-methylindene (I) ($[\alpha]_D^{18}$ +189.1°, *c* 1.2, $C_6H_6$, 93.2% *) [5] with $Et_2NSnMe_3$ in $C_6H_6$ yields (+)-(3-methylindenyl)-trimethyltin (II) ($[\alpha]_D^{18}$ +231°, *c* 4.2, $C_6H_6$) [12]. Since the signs of optical rotation of I and II are the same and the $Me_3Sn$ group has the greatest refraction [7] one may conclude, on the basis of Bruster's rule [8], that I and II have similar stereochemical configurations. The retention of Cotton effects' signs, observed in the DOR spectra is the supporting evidence.

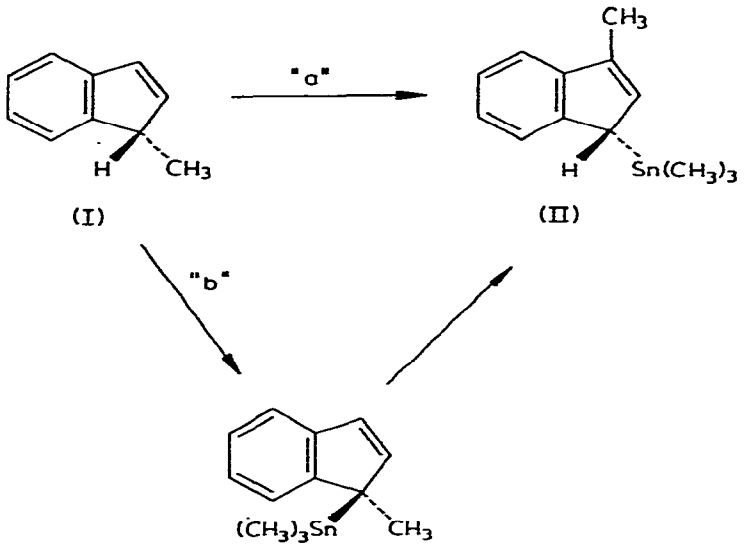
Unfortunately, direct determination of the stereospecificity of the formation of II is not possible because optical characteristics of enantiomer II are unknown. However the comparison of $[M]_D$ values, obtained experimentally, with those calculated by the BR—MR method [7] shows that the stereospecificity of the reaction may be as high as 90%.

The observed stereospecificity of the reaction with the transition of the chiral center of the molecule allows no adequate conclusion to be made as to the nature of the reaction mechanism.

The reaction may proceed by two pathways: as a one-step $S_E2$ mechanism "a" (with the transfer of the reaction center); or as a two-step mechanism "b" which includes a metallation step and (1.3) sigmatropic rearrangement of (1-

* The content of *S*-(I) is determined from specific rotation values of β-phentlbutyric acid used in the synthesis of I ($[\alpha]_{D\,exp}$ +50.5°, $[\alpha]_{D\,max}$ +58.5° [6]).

methylindenyl-1)trimethyltin to the more stable isomer II [9].




Note that in the case of mechanism "b" the metallation must proceed with retention of stereochemical configuration at the carbon atom and the rearrangement (III → II) must be realized as an intramolecular supraface process *.

The organotin compound II is stereochemically unstable, save in solutions of low polar solvents. Thus the racemisation is only 15% in DME after 24 h, yet in the presence of HMPTA it is very fast ($k_1^{18}$ 1.7 $10^{-5}$ $s^{-1}$, [$C_{10}H_9SnMe_3$] 3.99 $10^{-2}$ *M*, [HMPTA] 2.30 $10^{-2}$ *M*). We suppose that this stereochemical result is due to the ionisation of II in the presence of HMPTA with formation of solvated ion-pairs, which return to the initial state with racemisation as in the case of carbocationic ion-pairs [11].

## References

1 K. Sisido, S. Kozima and K. Takisawa, Tetrahedron Lett., (1967) 33.
2 F.R. Jensen and D.D. Davis, J. Amer. Chem. Soc., 93 (1971) 4047.
3 J. Hudec, J. Chem. Soc. Perkin I, (1975) 1020.
4 M. Gielen and H. Mokhtar-Jamaï, Bull. Soc. Chim. Belg., 84 (1975) 197.
5 G. Bergson and A.-M. Weidler, Acta Chem. Scand., 18 (1964) 1483.
6 D.J. Cram, J. Amer. Chem. Soc., 74 (1952) 2137.
7 D.D. Davis and F.R. Jensen, J. Org. Chem., 35 (1970) 3410.
8 J.H. Brewster, J. Amer. Chem. Soc., 81, (1959) 5475, 5483.
9 A. Davison and P.E. Rakita, J. Organometal Chem., 23 (1970) 407.
10 R.B. Larabee, J. Organometal. Chem., 74 (1974) 313.
11 I.P. Beletskaya, Usp. Khim., 44 (1975) 2205.
12 K. Jones and M.F. Lappert, J. Organometal. Chem., 3 (1965) 295.

* The rearrangement is an example of a metallotropic transformation well known for the indenyl derivatives of tin [10].