

Preliminary communication

STEREOSELECTIVE TRANSFORMATIONS OF THE OPTICALLY-ACTIVE TRIORGANOTIN HYDRIDES INTO OPTICALLY-ACTIVE TETRAORGANOTIN COMPOUNDS

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, Bruxelles (Belgium)

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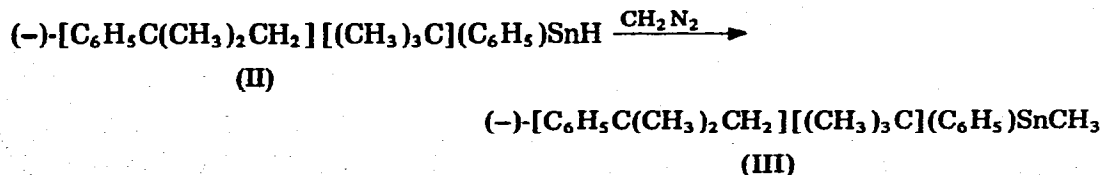
Summary

(-)-*t*-Butylneophylphenyltin hydride reacts with diazomethane to give (-)-*t*-butylmethylneophylphenyltin, while (-)- or (+)-methylneophylphenyltin hydrides add to the double bond of bifluorenylidene to give (-)- or (+)-bifluorenylmethylneophylphenyltin, respectively.

Triorganotin hydrides are optically stable for days: a benzene solution of methylneophylphenyltin hydride (I) loses about 50% of its optical activity in 17 days at room temperature [1]. *t*-Butylneophylphenyltin hydride (II) racemizes ca. twice as slowly. Neat, in a freezer (-22°C), the optical activity of both hydrides is practically unchanged after two weeks. Tetraorganotin compounds are optically stable for several years [2].

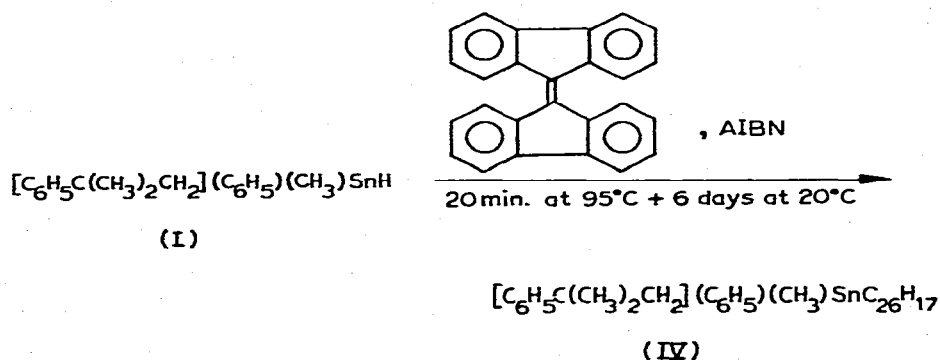
We have thus examined the optical activity of tetraorganotin compounds synthesized from the optically active triorganotin hydrides I and II which have been prepared by asymmetric reduction of the corresponding chlorides [1].

(-)-II with $[\alpha]_{365\text{nm}}^{30^\circ\text{C}} -0.89 \pm 0.04^\circ$ (*c* 12.3 in C₆H₆) has been transformed into (-)-*t*-butylmethylneophylphenyltin (III) with $[\alpha]_{365\text{nm}}^{30^\circ\text{C}} -1.50 \pm 0.13^\circ$ (*c* 3.67 in CCl₄) by a reaction with diazomethane in ether in the presence of copper [3]:



The NMR spectrum of III is identical to that of an authentic racemic sample prepared from methylneophylphenyltin chloride and t-butyllithium [4].

(-)-I with $[\alpha]_{365\text{nm}}^{30^\circ\text{C}} -0.70 \pm 0.05^\circ$ (c 7.89 in C_6H_6) reacts with bifluorenylmethylenephene in the presence of AIBN and is converted into (-)-bifluorenylmethylneophylphenyltin (IV) with $[\alpha]_{365\text{nm}}^{30^\circ\text{C}} -0.39 \pm 0.12^\circ$ (c 4.15 in CCl_4). Analogously, (+)-I with $[\alpha]_{\text{D}}^{30^\circ\text{C}} +1.75 \pm 0.02^\circ$ (c 20.78 in C_6H_6) is transformed into (+)-IV with $[\alpha]_{\text{D}}^{30^\circ\text{C}} +0.79 \pm 0.11^\circ$ (c 4.55 in CCl_4). The NMR spectra of both optically active compounds are identical to those of an authentic racemic sample of IV.



Furthermore, (-)-II with $[\alpha]_{\text{D}}^{30^\circ\text{C}} -0.84 \pm 0.03^\circ$ (c 14.68 in C_6H_6) reacts with LiAlD_4 in ether at room temperature; after 18 h, more than 90% can be recovered which contain 80% of the corresponding deuteride and 20% of II. The optical activity of this mixture is only 20% of the initial optical activity of II, suggesting that the H-D exchange may proceed with racemization.

Acknowledgements

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References

- 1 M. Gielen and Y. Tondeur, *J. Organometal. Chem.*, in press.
- 2 H. Mokhtar-Jamali and M. Gielen, *Bull. Soc. Chim. France* 9B (1972) 32; M. Gielen and H. Mokhtar-Jamali, *Annals N.Y. Acad. Sci.*, 239 (1974) 208; *Bull. Soc. Chim. Belg.*, 84 (1975) 197.
- 3 M. Lesbre and R. Buisson, *Bull. Soc. Chim. France*, (1957) 1204.
- 4 M. Gielen and H. Mokhtar-Jamali, *Bull. Soc. Chim. Belg.*, 84 (1975) 1037.