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STEREOCHEMISTRY AT TIN AND MECHANISM OF THREE CLEAVAGE REACTIONS OF CARBON—TIN BONDS *

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Summary

The cleavages of the trityl—tin bond by $NaFe(CO)_2Cp$, $LiBHEt_3$ and Ph_3SnLi are not stereoselective. This is explained in terms of a one-electron transfer mechanism leading to a triorganostannyl radical which can undergo inversion before reacting with another radical to give the product.

Introduction

Tetraorganotin compounds [2], triorganostannyl-iron complexes [3], triorganotin hydrides [4] and hexaorganoditin compounds [5] are optically stable for long periods. Therefore, it is in principle possible to determine whether reactions transforming tetraorganotins into the three other types of organotin compounds are stereoselective. Moreover, racemic tetraorganotin compounds can be resolved by column chromatography on chiral microcrystalline triacetylcellulose, and several optically-active tetraorganotin compounds are readily available [2]. It is also known that the trityl—tin bond is easily cleaved by dicarbonylcyclopentadienylferrate [1] and by lithium aluminum hydride [4]. In view of these observations we studied cleavages of the trityl—tin bond of methylneophenyltrityltin [1] by $NaFe(CO)_2Cp$, $LiSnPh_3$ and $LiBHEt_3$ ***.

The reactions of $Cp(CO)_2Fe^-$ with alkyl halides or pseudo-halides RX can occur either via the classical S_N2 mechanism [6] or via an electron transfer

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*** Cp stands for cyclopentadienyl, Ph, for phenyl and Et, for ethyl.

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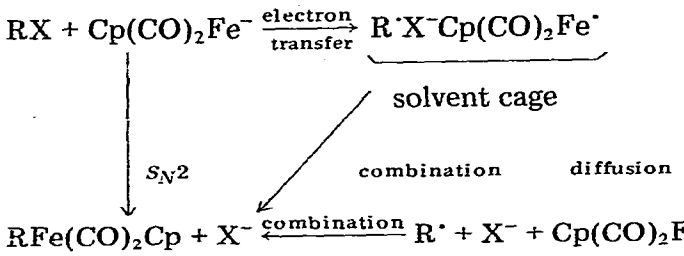
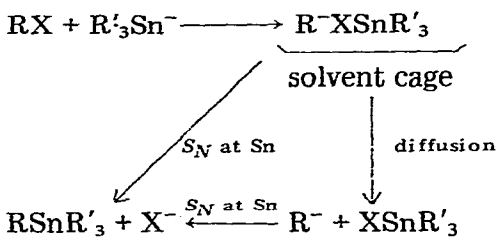
mechanism [7]:



The low stereoselectivity obtained for the reaction of $Cp(CO)_2Fe^-$ with chiral methyl-1-naphthylphenylchlorosilane has been explained similarly by the competition between a one electron-transfer mechanism (followed by a recombination of radicals proceeding with retention of configuration) and a S_N2 reaction proceeding with inversion of configuration [8].

A third mechanism has been proposed for the reaction of R'_3Sn^- with RX [9]:



Results and discussion

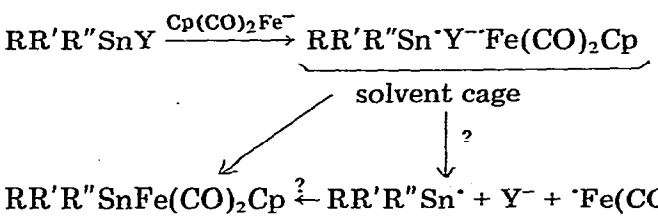
Cleavage of the trityl—tin bond by dicarbonylcyclopentadienylferrate

(—)-Methylneophylphenyltrityltin, (—)-I [2] was converted into racemic (methylneophylphenylstannyl)dicarbonylcyclopentadienyliron, (±)-II, when treated with sodium dicarbonylcyclopentadienylferrate in THF for 15 h.

$$Me(PhMe_2CCH_2)PhSnCPh_3 \xrightarrow[THF/15\ h]{Na^+Cp(CO)_2Fe^-} Me(PhMe_2CCH_2)PhSnFe(CO)_2Cp$$

((—)-I, $[\alpha]_D^{30°}$ —30.2°) ((±)-II, (83%))

The absence of optical activity in compound II may be due to the operation of a mechanism analogous to that suggested by San Filippo's [7], giving a triorganostannyl radical which can undergo inversion before it is quenched by $Cp(CO)_2Fe^·$ to give II.



A similar explanation was offered for the absence of stereoselectivity at tin for the cleavage of the cobalt—tin bond by means of $Cp(CO)_2Fe^-$ [1].

Cleavage of the trityl—tin bond by triphenylstannyllithium

Racemic I reacts with Ph_3SnLi made from Ph_3SnCl and Li in THF to give after 3 h a mixture of 52% $[Me(PhMe_2CCH_2)PhSn]_2$ (52%) (III), $Me(PhMe_2CCH_2)$-$PhSnSnPh_3$ (37%) (IV) and hexaphenylditin (51%), plus 5% unreacted I. Traces of lithium metal may be present when Ph_3SnLi is prepared in this way, and so we carried out a similar experiment with Ph_3SnLi prepared from Ph_3SnH and $LiN(CHMe_2)_2$. In this case (+)-I was converted after 4 h in THF into optically inactive III (50%), racemic IV (30%) and hexaphenylditin (54%).

An analogous one-electron-transfer mechanism accounts for the absence of stereoselectivity for this substitution and for the presence of comparable amounts of the three possible hexaorganoditin compounds:

$$RR'R''SnY \xrightarrow{Ph_3Sn^-} \underbrace{RR'R''Sn^{\cdot}Y^{-\cdot}SnPh_3}_{\text{solvent cage}}$$

$$\left.\begin{array}{l} RR'R''Sn{-}SnRR'R'' \\ RR'R''Sn{-}SnPh_3 \\ Ph_3Sn{-}SnPh_3 \end{array}\right\} \leftarrow RR'R''Sn^{\cdot} + Y^- + {}^{\cdot}SnPh_3$$

The three posible hexaorganoditins are also formed when triorganostannyl-cobalt complexes [1] and triorganotin chlorides react with Ph_3Sn^-.

Cleavage of the trityl—tin bond by lithium triethylhydridoborate

The trityl—tin bond of (+)-I, $[\alpha]_D^{30^\circ} = +30.0^\circ$ was cleaved by $HBEt_3^-$ in THF and after 4 h, 63% optically inactive III was obtained. No trace of methylneophylphenyltin hydride could be detected by TLC. This result is analogous to that described by Tondeur [4]:

$$(+)\text{-}Me(PhMe_2CCH_2)(Me_2CH)SnCPh_3 \xrightarrow[THF]{LiAlH_4} [Me(PhMe_2CCH_2)(Me_2CH)Sn]_2$$

$([\alpha]_D^{30^\circ} = +1.76^\circ)$ optically inactive

Triethylhydridoborate also cleaves the carbon—cobalt bond to give a hexaorganoditin [1]. The outcome of the reactions of $RR'R''Sn{-}Y$ compounds ($Y = CPh_3$ or $Co(CO)_3PPh_3$) with $HBEt_3^-$ are easily explained if $RR'R''SnY$ is assumed to react with triethylhydridoborate to give $RR'R''Sn^-$ and HY with the formed $RR'R''Sn^-$ reacting with $RR'R''SnY$ as in the scheme given above.

Experimental

All substitution reaction were performed under nitrogen in freshly distilled THF.

Reaction of (—)-I with $NaFe(CO)_2Cp$

5 ml of 4×10^{-2} *M* $NaFe(CO)_2Cp$/THF were added to a solution of 100 mg

(0.17 mmol) of (—)-I, $[\alpha]_D^{30}$ —30.2 (c = 0.82, Et_2O) in 5 ml of THF. After 15 h, the mixture was worked up as usual and purified by chromatography on a small Al_2O_3 column (ϕ: 1 cm; l: 20 cm; elution with PhH/pet. ether —1/2): 75 mg (83.5%) II ($[\alpha]_\lambda^{30}$ = 0.00 for λ = 589, 578, 546 nm) and 30 mg Ph_3CH were obtained.

Reaction of (±)-I with $LiSnPh_3$

3 ml of 0.37 *M* $LisnPh_3$ (prepared as described by Tamborski [10]) were added to 600 mg (1 mmol) of I dissolved in 10 ml of THF. The mixture immediately became blood-red. After 3 h, hydrolysis with wet ether changed the color to yellow. After work up, chromatography on SiO_2 (ϕ: 2.8 cm; l: 80 cm; elution with PhH/pet. ether 1/5—1/2) gave four fractions: 221 mg (91%) Ph_3CH; 290 mg, containing some starting product (5%) from which 180 mg (52%) pure III [1] could be obtained; 260 mg IV (37%), and 177 mg (51%) Ph_6Sn_2.

Reaction of (+)-I with $LiSnPh_3$

1.3 ml of $LiSnPh_3$/THF prepared as described in ref. 1 were added to 100 mg (0.17 mmol) of (+)-I, $[\alpha]_D^{30}$ = +30.0 (c = 0.56/Et_2O) dissolved in 5 ml of THF. The mixture immediately turned blood-red. After 4 h work up as above gave 36 mg (88%) Ph_3CH, 29 mg (50%) III, 35 mg (30%) IV and 38 mg (54%) Ph_6Sn_2. Both III and IV showed $[\alpha]_\lambda^{30}$ = 0.00 for λ = 589, 578, 546, 436, 365 nm (c = 0.45, Et_2O).

Reaction of (+)-I with $LiEt_3BH$

To a solution of 147 mg (0.25 mmol) of (+)-I, $[\alpha]_D^{30}$ = +30.0 in 2 ml of THF was added 0.300 ml of a 1.0 *M* solution of $LiEt_3BH$ in THF. The color changed from colorless to yellow, orange, and then orange-red during about 1 h. After 4 h, TLC (SiO_2, PhH/pet. ether, 1/3) showed two spots, with R_F = 0.53 (Ph_3CH) and 0.49 III. After hydrolysis with wet ether, chromatography on SiO_2 gave 46 mg Ph_3CH and 54 mg (63%) III, $[\alpha]_\lambda^{30}$ = 0.00 (λ = 589 to 365 cm, c = 0.91, C_6H_6).

Reaction of methylneophylphenyltin chloride with $LiSnPh_3$

A solution of 24 mmol $LiSnPh_3$, as in ref. 10, in 66 ml THF was added in 30 min to a solution of 9.0 g (24 mmol) of methylneophylphenyltin chloride in 50 ml of THF. After 2 h the mixture was poured onto 200 g of ice, Et_2O was added, and the ether extract was worked up in the usual way. Drying over Na_2SO_4 gave a precipitate (1.8 g) of Ph_6Sn_2. The products were separated by chromatography (SiO_2; ϕ: 3 cm; l: 90 cm PhH/pet. ether 1/5 to 1/1): 3.3 g (38%) III, 5.5 g (32%) IV and a further 1.8 g of Ph_6Sn_2 (total yield: 43%) were obtained,

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