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ORGANOMETALLIC COMPOUNDS

LXXII *. REACTIONS OF RACEMIC TETRAORGANOTIN COMPOUNDS WITH BUTYLLITHIUM AND WITH LITHIUM ALUMINUM HYDRIDE

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Summary

Racemic methylneophylphenyltrityltin (I) reacts with an excess of butyllithium to give dibutylmethylneophyltin (II) in high yield, whereas bifluorenyl-9-ylmethylneophylphenyltin is converted with an excess butyllithium into butylmethylneophylphenyltin (III) together with some (II). This shows that the phenyl is cleaved off as easily as the trityl group but less than the bifluororenylyl group. Methylphenyl(phenylethynyl)(2-phenylpropyl)tin and phenylethynyltrimethyltin react with $LiAlH_4$; the phenylethynyl—tin bond is cleaved but the formed phenylacetylene and organotin hydride react together to give the expected adduct. Bifluorenyl-9-ylmethylneophylphenyltin is converted with $LiAlH_4$ into 1,2-dimethyl-1,2-dineophyl-1,2-diphenylditin.

Introduction

Chiral tetraorganotin compounds are optically stable for long periods [2], and react readily with electrophiles such as halogens or hydrogen halides to give optically unstable triorganotin halides [3]. The stereochemistry at tin of these cleavage reactions of carbon—tin bonds cannot thus be easily determined [3].

Tetraorganotin compounds are known to react with organolithium reagents. Even in 1941, Gilman reported the reaction of tetraphenyltin with butyllithium

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* For part LXXI, see ref. 1.

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to give tetrabutyltin in about 90% yield [4]. Many reports have appeared since of reactions in which tetraorganotin compounds are converted by organolithium reagents into other tetraorganotin compounds [5]. These reactions have been used successfully to prepare organolithium reagents which are difficult to make by the conventional methods [6,7]. Seyferth has shown that only one methyl group of tetramethyltin is replaced by a butyl group if 2.5 equivalents of butyllithium are used [8]. Butyltrimethyltin can be converted into dibutyldimethyltin by the same reagent [7].

Results and discussion

We wished to determine whether the replacement of an organic ligand of a racemic tetraorganotin compound is selective enough to be studied with optically active tetraorganotins.

Reactions of methylneophylphenyltrityltin (I) with butyllithium

Methylneophylphenyltrityltin (I) reacts with an excess of butyllithium in diethyl ether to give dibutylmethylneophyltin (II) in 91% yield. This reaction is not suitable for studying the stereochemistry of the replacement of either the phenyl or trityl group by butyl because both are substituted in these circumstances.*. When the same reaction is carried out in the presence of only one equivalent of butyllithium, only 30% of I reacts and butylmethylneophylphenyltin (III) and compound II are obtained in about 2% yield; some mono-substituted product is formed, but is contaminated with the disubstituted product and is obtained in such low yields that we did not undertake an analogous study on optically active I.

Reaction of bifluorenyl-9-ylmethylneophylphenyltin (IV) with butyllithium

Bifluorenyl-9-ylmethylneophylphenyltin (IV) [10,11] reacts with an excess of butyllithium in diethyl ether to give 41% (III) together with 8% of II. Dibifluorenylyl (33%) and bifluorenylidene (16%) are also present. The bifluorenylyl group is clearly cleaved off more easily than the phenyl group by butyllithium.

If the same reaction is carried out in the presence of only one equivalent of butyllithium, 69% of IV is recovered and 5% III is obtained together with 10% bifluorenylidene. No dibifluorenylyl can be detected.

Reactions of tetraorganotin compounds with $LiAlH_4$

Triorganotin hydrides like tetraorganotin compounds are optically stable for long periods [11,12]. It would thus be of interest to find a way of transforming a tetraorganotin compound into a triorganotin hydride. (Stereoselective transformations of triorganotin hydrides into tetraorganotin compounds have been reported [10].)

Some functionally-substituted organotin compounds are known to react with

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* Methylneophylphenyltin chloride (X) reacts with an excess butyllithium to give 10% of the expected III together with 53% of II.

$LiAlH_4$ to give the corresponding triorganotin hydrides:

$$R_3SnCH_2X \xrightarrow{LiAlH_4} R_3SnH$$

X = CN [13], COOEt [13], COOMe [14], COPh [15]

Petrov [16] reported the cleavage of another carbon—tin bond by lithium aluminum hydride:

$$Et_3Sn{-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow{LiAlH_4} Et_3SnH$$

while Lorberth [17] obtained trimethyltin hydride and the dibutylphenylethynylaluminum dimer from phenylethynyltrimethyltin (V) and dibutylaluminum hydride. Thus, we prepared some alkynyl triorganotin compounds and studied their reactions with $LiAlH_4$.

Phenylethynyltrimethyltin (V) does react with $LiAlH_4$. A mixture of compounds is obtained which are the products of addition of trimethyltin hydride to the phenylacetylene formed by the initial cleavage of the phenylethynyl—tin bond by $LiAlH_4$. Methylphenyl(phenylethynyl)(2-phenylpropyl)tin (VI) reacts analogously with $LiAlH_4$. Furthermore, when methylphenyl (2-phenylpropyl)-tin hydride (VII) is treated with phenylacetylene, at least two new organotin compounds are formed; the NMR spectra show that the SnH and $SnCH_3$ signals of VII disappear, and that at the same time two new signals appear in the $SnCH_3$ region. Olefinic protons also appear. The phenylethynyl group is thus not a very good group for studying the replacement of an organic group bound to tin by a hydride ion.

When(+)-methylneophylisopropyltrityltin reacts with $LiAlH_4$, optically inactive $[(PhMe_2CCH_2)(Me_2CH)MeSn]_2$ is formed [11]. Bifluorenyl-9-ylmethylneophylphenyltin (IV) reacts analogously with $LiAlH_4$. When 50% of IV has disappeared, it has been almost quantitatively transformed into $[(PhMe_2CCH_2)PhMeSn]_2$ (VIII). Only traces of methylneophylphenyltin hydride (IX) can be detected by TLC. Product IX might come from the reaction of VIII with $LiAlH_4$; hexabutylditin is known to react with $LiAlH_4$ to give 4% of tributyltin hydride after 18 h at 35°C [18]. We also confirmed that a mixture of IV and IX does not give any new species when kept in ether at room temperature or neat at 60°C during 4 h.

Experimental

Reaction of butyllithium with phenyltrimethyltin (XI)

A mixture of 10 mmol of freshly prepared BuLi in ether are added to 2 g (8.3 mmol) phenyltrimethyltin (XI) in 6 ml of Et_2O is left overnight at room temperature, then hydrolyzed and worked up as usual. The oil obtained is chromatographed on SiO_2 (elution with n-pentane) to yield 51% of Bu_2SnMe_2 (XII) 30% of $BuSnMe_3$ (XIII), and 19% of starting material.

When one equivalent of BuLi is left for 2 h under reflux with XI, 40% of XI is recovered and 58% of XIII obtained. Only traces of XII are detected by TLC.

Reaction of phenyllithium with trityltrimethyltin (XIV)

A solution of 1.5 mmol of freshly prepared PhLi in ether is added to a suspension of 0.25 g (0.61 mmol) of XIV in 2 ml Et_2O was kept for 24 h at room temperature, then hydrolysed and worked up as usual. No starting material can be detected by NMR but triphenylmethane (100%), XI (46%), dimethyldiphenyl tin (XV) (37%), and methyltriphenyltin (XVI) (7%) are present.

Reaction of butyllithium with 2-phenylpropyltriphenyltin (XVII)

A solution of 18 mmol of freshly prepared BuLi in Et_2O is slowly added to 2 g (4.27 mmol) of XVII in 10 ml Et_2O. After 10 h at room temperature and 2 h under reflux, the reaction mixture is hydrolyzed and worked up as usual to give 1.97 g of a colorless liquid which is chromatographed on SiO_2 (petroleum ether, b.p. 30—60°C) and gives 1.68 g (96%) tributyl(2-phenylpropyl)tin (XVIII). ($R_f = 0.46$, $n_D^{20} = 1.5096$ [lit.: 1.511 [19]]; elemental analysis. Found: C, 61.81; H, 9.32. $C_{21}H_{38}Sn$ calcd.: C, 61.66; H, 9.30%. Monoisotopic M.S. (70 eV) [*m/e*, intensity, fragment ion]: 120, 5, Sn^+; 121, 15, SnH^+; 135, 1.5, $MeSn^+$; 177, 7, $BuSn^+$; 179, 30, $BuSnH_2{}^+$; 197, 8, $PhSn^+$; 235, 6, Bu_2SnH^+; 239, 3, $PhCHMeCH_2S$ 255, 0.2, $BuPhSnH^+$; 296, 3, $Bu(PhCHNeCH_2)Sn^+$; 312, 0.2, Bu_2PhSnH^+; 353, 22 $Bu_2(PhCHMeCH_2)Sn^+$).

Reaction of BuLi with $Me(PhMe_2CCH_2)PhSnCPh_3$ (I)

A solution of 50 mmol freshly prepared BuLi in Et_2O is added to a suspension of 1 g of I in 5 ml Et_2O at 0°C. After one h at room temperature, the mixture is red. After one night at room temperature and 2 h under reflux it is hydrolyzed, worked up usual, and chromatographed on SiO_2 (eluent: n-pentane). 590 mg of a colorless liquid (90.7%) are obtained, which is identified as II (R_f = 0.4; b.p.: 62°C/0.95 torr; n_D^{19}: 1.5135. Elemental analysis. Found: C, 59.96; H, 8.95, $C_{19}H_{34}Sn$ calcd.: C, 59.89; H, 8.93%. Monoisotopic M.S. (70 eV): 120, 1.5, Sn^+; 121, 3, SnH^+; 134, 0.4, $SnCH_2{}^+$; 135, 7.8, $MeSn^+$; 149, 0.6, $MeSnCH_2{}^+$; 151, 0.8, Me_2SnH^+; 177, 1.3, $BuSn^+$; 179, 0.3, $BuSnH_2{}^+$; 193, 5, $MeBuSnH^+$; 197, 6.3, $PhSn^+$; 213, 11, $MePhSnH^+$; 235, 0.5, Bu_2SnH^+; 249, 1.6, $MeBu_2Sn^+$; 253, 2, $PhMe_2CCH_2Sn^+$; 269, 7.6, $MePhBuSn^+$ or $Me(PhMe_2CCH_2)SnH^+$; 291, 0.4, $Bu_2HSnCH_2CMe_2{}^+$; 311, 1.3, $PhBu_2Sn^+$ or $PhMe_2CCH_2BuSnH^+$; 325, 42, $Me(PhMe_2CCH_2)BuSn^+$; 367, 4.6, $(PhMe_2CCH_2)Bu_2Sn^+$ with metastable peaks at 223 (325 → 269) and 169 (269 → 213). The 270 MHz ^1H NMR spectrum of II shows a CH_3Sn signal at —0.234 ppm [$^2J(^{119/117}SnCH_3) = 49.5/46.9$ Hz], a neophylic CH_3 signal at 1.361 plus signals around 1.31, 0.85, 0.56 and 7.1 ppm).

If one equivalent of BuLi is used instead of an excess, NMR shows that only 30% of I has reacted after one night at room temperature and 2 h under reflux. The obtained oil is chromatographed on SiO_2 (elution with toluene/pet. ether 40°C, 20/80) giving 10.8 mg II and 14.3 mg III. Finally, 657 mg of a mixture of Ph_3CH and starting material are obtained.

Reaction of BuLi with bifluorenyl-9-ylmethylneophylphenyltin (IV)

To a solution of 300 mg (0.44 mmol) of IV in 1 ml Et_2O, is added one equivalent of freshly prepared BuLi in the same solvent. The mixture becomes red. After two h, TLC still shows the presence of IV. The mixture is kept at room temperature overnight then refluxed for 2 h and hydrolyzed. After the usual work up, 310 mg of an orange solid is obtained and chromatographed on SiO_2 with petroleum ether, b.p. 40°C/toluene, 80/20. 8 mg (4.5%) of III are first obtained, then 87 mg of a red solid, which after recrystallization from i-PrOH, is identified as bifluorenylidene (IR and mixed m.p.). Finally, 206 mg (68.7%) of the starting material IV can be recovered.

With an excess of butyllithium (2.37 mmol BuLi compared with 0.74 mmol of IV), 8.1% of II is first obtained, followed by 41.2% of III, 16% of bifluorenylidene and 32.9 of dibifluorenyl (m.p. 244—246°C after recrystallization from EtOH, lit. 246°C [23]).

Reaction of BuLi with methylneophylphenyltin chloride (X)

A solution of 12 mmol of freshly prepared BuLi in Et_2O is added dropwise to a solution of 2 g (5.3 mmol) of (X) in 10 ml of Et_2O. After one night at room temperature and 2 h under reflux, the mixture is hydrolyzed. The usual work up yields 2.14 g of a yellow liquid. Chromatography on SiO_2 (eluent, petroleum ether, b.p. 40°C) gives 1.07 g of a colorless liquid, which is distilled and is identified as II (53.5%). Progressive replacement of petroleum ether by toluene allows isolation of a second fraction (210 mg), which is compound III (10%).

Reaction of $LiAlH_4$ with phenylethynyltrimethyltin (V)

After 2 h reflux in ether of a mixture of $LiAlH_4$ and V followed by hydrolysis, the NMR spectrum shows that V has disappeared and that the *cis* and *trans* organotin compounds resulting from the addition of Me_3SnH to phenylacetylene [$Me_3Sn(CH{=}CHPh)$] [20] have been formed.

Reaction of $LiAlH_4$ with bifluorenyl-9-ylmethylneophylphenyltin (IV)

To a suspension of 76 mg of $LiAlH_4$ in 2 ml ether is added a solution of 100 mg (0.15 mmol) of IV in 2 ml ether. After 2 h the mixture has become brown. After 2 h more, the mixture is hydrolysed and worked up as usual. NMR spectroscopy shows that 50% of the starting tetraorganotin compound has disappeared and has been converted into $(Me(PhMe_2CCH)PhSn)_2$ (VIII) (92%), dibifluorenylyl, and bifluorenylidene. TLC shows the presence of traces of methylneophylphenyltin hydride (IX).

Synthesis of methylphenyl(phenylethynyl)(2-phenylpropyl)tin (VI)

This compound was prepared by the organolithium route [21]. The 60 MHz NMR spectrum of VI (CCl_4 solvent) shows two CH_3Sn signals at 0.32 and 0.36 ppm (intensities 1 : 0.93) ($^2J(^{119/117}SnCH_3)$ = 58.8/56.4 Hz) corresponding to the *erythro* and *threo* isomers.

Synthesis of phenylethynyltrimethyltin (V)

Phenylethynyltrimethyltin (V) was prepared similarly, (yield: 35%; b.p. 73—74°C/0.9 torr). Its NMR spectrum is identical to that described by Cadiot (40% yield; b.p. 107°C/1.5 torr [22]).

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