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Reaction of Bis(phenylethynyl)itterbium with Tetraphenylantimony Halides

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Abstract—Phenylethynyl itterbium derivative $(PhC{\equiv}C)_2Yb(THF)_2$ reacts with tetraphenylantimony halides in tetrahydrofuran (THF) at room temperature to form triphenylantimony, phenylacetylene, benzene, and phenylethynylitterbium $PhC{\equiv}CYbX(THF)_4$ and itterbium $YbX_2(THF)_4$ halides; X = Cl, Br, I. The reduction of the antimony derivative is accompanied with the generation of phenyl and phenylethynyl radicals.

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We have reported previously [1] on the reaction of bis(phenylethynyl)itterbium with trimethylsilicon, triphenylgermanium and triphenyltin halides in THF at room temperature leading basically to formation of corresponding non-symmetrical organoelement derivative $R_3EC{\equiv}CPh$ (the products of cross-coupling, E = Si, Ge, Sn) and phenylethynyl itterbium and itterbium(II) chlorides. In this work we aimed at the study of reactivity of bis(phenylethynyl)itterbium toward tetraphenylantimony halides Ph_4SbX (X = Cl, Br, I).

We established that bis(phenylethynyl)itterbium readily reacts with tetraphenylantimony halides (in 1 : 2 ratio) in THF at room temperature. The reaction started just after mixing of the reagents but for completion the mixture was kept for 24 h. From the data listed below is seen that the main products are triphenylantimony, phenylacetylene, benzene and halides of phenylethynyl itterbium and itterbium(II).

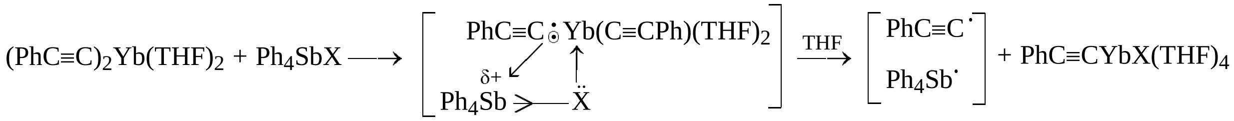
The compounds $YbX_2(THF)_4$ are diamagnetics, the magnetic moment of $PhC{\equiv}CYbX(THF)_4$ is about 0.3 MB (X = Cl, Br, I). In the case of trivalent itterbium derivative the moment is 3.8 to 4.3 MB [2]. Hence in the process of oxidation the state of oxidation of itterbium do not practically change. It is noteworthy that in contrast to phenylethynyl itterbium derivatives the bis(pentamethylcyclopentadienyl)itterbium does not react with trimethyl silicon chloride but is readily oxidized by haloalkanes and iodobenzene to trivalent state [3].

In the reactions studied by us the expected product of cross-coupling tetraphenylantimony phenylacetylenide was not detected. This fact points to another character of the reaction, in contrast to the elements of IVA group organohalides. The high yield of phenylacetylene and benzene in the reaction of bis(phenylethynyl)itterbium with tetraphenylantimony halides (see the table) points to participation in the process of phenylethynyl and phenyl radicas that react with THF abstracting hydrogen atoms from the latter. It is very probable that these reactions follow to the mechanism of single-electron transfer (see the scheme).

Recombination of the radical pair formed does not occur because it would not result in the formation of a stable compound [4, 5]. Moreover, phenylethynyl radical could react with coordinated THF still being included to the **A** complex. Stabilization of the metal-

The products of reaction of bis(phenylethynyl)itterbium with Ph_4SbX (1 : 2) in THF at room temperature for 24 h, mol per 1 mol of $(PhC{\equiv}C)_2Yb(THF)_2$

X	Ph_3Sb	$PhC{\equiv}CH$	PhH	$PhC{\equiv}CYbX(THF)_4$	$YbX_2(THF)_4$
Cl	1.83	1.15	1.01	0.70	0.25
Br	1.61	1.65	1.15	0.32	0.67
I	1.85	1.17	1.28	0.71	0.29



A

X = Cl, Br, I.

centered radical proceeds via splitting phenyl radical off which affords triphenylantimony. In the following process of the phenyl and phenylethynyl radicals transformation the state of the carbon atoms oxidation with unpaired electron grows from –1 to 0. A similar process of the of phenyl radical formation takes place in the reaction of sodium tetraphenylboronate with mixed organomercury, organotin and organolead compounds [6]. Earlier was reported [7] on the reduction of triphenylantimony diacetate to triphenylantimony and biphenyl in the reaction with phenylitterbium iodide.

As seen from the table, among the used tetraphenylantimony halides the most active is bromide. This is probably a result of the Sb–Br bond feature which is less strong than Sb–Cl but more polar than Sb–I [8]. These factors affect the step of the single-electron transfer. The phenylethynyl itterbium halide formed exerts in part further dealkynylation affording itterbium halide $YbX_2(THF)_4$. Thus, itterbium phenylethynyl derivative under the action of tetraphenylantimony halides exerts stepwise dealkynylation proceeding via formation of free radicals.

EXPERIMENTAL

All operation with the readily oxidizing and hydrolyzing compounds were performed in sealed under vacuum ampoules with carefully dried and degassed solvents. IR spectra were taken on an IKS-25 spectrometer, the samples were prepared under argon atmosphere as suspensions in Vaseline oil. Magnetochemical measurements were performed according to [9].

Phenylethynyl itterbium derivatives were prepared by the reaction of itterbium diiodide with sodium phenylethynylate in THF [10]. Tetraphenylantimony chloride and bromide were synthesized by known procedure [4].

Melting (decomposition) points of the initial and obtained compounds were determined in sealed capillary tubes (values are given without correction).

Reaction of $(PhC{\equiv}C)_2Yb(THF)_2$ with Ph_4SbCl. To a solution of 0.53 g $(PhC{\equiv}C)_2Yb(THF)_2$ in 15 ml of THF was added 0.95 g of Ph_4SbCl dissolved in 5 ml of THF. The reaction rate was the same as the rate of mixing of the reagents, and in the course of the process the color was changing from dark violet to light brown and itterbium(II) chloride precipitate dropped. For completion, the reaction mixture was kept for 24 h at room temperature. From the reaction mixture 0.10 g of $YbCl_2(THF)_4$ was isolated, yield 25%, as gold-brown substance, decomp. >300°C. Found, %: Yb 32.08; Cl 13.30. $C_{16}H_{32}Cl_2O_4Yb$. Calculated, %: Yb 32.51; Cl 13.34.

From the mother liquor the liquid reaction components were re-condensed in a vacuum to a trap cooled with liquid nitrogen. The GLC of the trapped material detected phenylacetylene 1.17 mmol and benzene 1.03 mmol.

Solid residue was triple washed with hexane (10 ml portions) and dried in a vacuum to constant weight. 0.42 g of $PhC{\equiv}CYbCl(THF)_4$ was isolated as brown amorphous substance insoluble in hexane, yield 70%, mp 175°C. Found, %: Yb 28.58; Cl 5.29. $C_{24}H_{37}\cdot ClO_4Yb$. Calculated, %: Yb 28.95; Cl 5.94. IR spectrum (Vaseline oil), ν, cm^{-1}: 2200 medium ($PhC{\equiv}C$); 2050 medium ($C{\equiv}C$); 1880 weak, 1790 weak, 1445 strong, 1380 strong, 1300 strong, 1070 medium, 1025 strong, 995 strong, 730 medium, 670 strong, 490 medium, and the adsorption bands at 1040 medium and 840 medium, of the coordinated THF.

From the hexane extracts the solvent was removed. The residue was Ph_3Sb (0.66 g), yield 91.5%, a light yellow low melting substance well soluble in THF, benzene and hexane. The product was identified by reaction with acetic acid in the presence of hydrogen peroxide (see below).

Reaction of $(PhC{\equiv}C)_2Yb(THF)_2$ with Ph_4SbBr. To a solution of 0.54 g of $(PhC{\equiv}C)_2Yb(THF)_2$ in 15 ml of THF was added 1.06 g of Ph_4SbBr dissolved in 5 ml of THF. Reaction proceeded like the described above.

The products obtained: (a) 0.43 g of $YbBr_2(THF)_4$. This compound changed its color from green to yellowish-green during its drying in a vacuum to constant weight (published data [11]: light green by color) decomp. >300°C, yield 67 %. Found, %: Yb 28.81; Br 27.01. $C_{16}H_{32}Br_2O_4Yb$. Calculated, %: Yb 27.85; Br 25.76.

(b) Phenylacetylene and benzene, 1.71 and 1.19 mmol, respectively.

(c) 0.22 g of PhC≡CYbBr(THF)$_4$, brown amorphous substance, insoluble in hexane, mp 185–190°C, yield 32 %. Found, %: Yb 24.18; Br 11.08. $C_{24}H_{37} \cdot BrO_4Yb$. Calculated, %: Yb 26.94; Br 12.46.

(d) Ph_3Sb 0.59 g. Yield 80.5%.

Reaction of (PhC≡C)$_2$Yb(THF)$_2$ with Ph_4SbI. To a solution of 0.52 g of (PhC≡C)$_2$Yb(THF)$_2$ in 15 ml of THF was added 1.11 g of Ph_4SbI dissolved in 5 ml of THF. Reaction proceeded similarly to the described above.

The substances obtained: (a) 0.20 g of $YbI_2(THF)_4$ as a yellowish-greenish substance (described [11] as pale yellowis-green crystals) decomp. >300°C, yield 29 %. Found, %: Yb 25.99; I 35.02. $C_{16}H_{32}I_2O_4Yb$. Calculated, %: Yb 24.19; I 35.52.

(b) Phenylacetylene (1.17 mmol) and benzene (1.28 mmol).

(c) PhC≡CYbI(THF)$_4$ (0.49 g), redish-brown amorphous substance, insoluble in hexane, mp 250°C, yield 71%. Found, %: Yb 24.93; I 18.25. $C_{24}H_{37} \cdot IO_4Yb$. Calculated, %: Yb 25.10; I 18.43.

(d) Ph_3Sb (0.65 g), yield 92.5%.

Determination of Ph_3Sb. To a solution of 0.51 g Ph_3Sb in 0.17 ml of anhydrous CH_3COOH was added 0.05 ml of 30% H_2O_2. Reaction proceeded with the rate of mixing of the reagents. Triphenylantimony diacetate formed quantitatively (0.68 g) as a precipitate. The latter was triple washed with hexane (3 ml portions) and dried, mp 211–213°C (published [4] 213–215°C).

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