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Phenylation of Organic Derivatives of Mercury, Silicon, Tin, and Bismuth with Pentaphenylantimony and Pentaphenylphosphorus

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Abstract — Pentaphenylantimony and -phosphorus react with arylmercury chlorides in toluene at room temperature to give diaryl derivatives of mercury in yields of up to 95%. The reactions of pentaphenylantimony and -phosphorus with silicon and tin halides involve arylation of the latter in yields of up to 79%. The products of the reaction of pentaphenylphosphorus with triphenylbismuth dihalides are tetraphenylphosphorus halides, triphenylbismuth, and halobenzene.

It is known that pentaarylantimony and pentaphenylbismuth effectively arylate organic derivatives of tin, antimony, and bismuth [1–7]. Continuing research into the arylating action of pentaphenyl derivatives of antimony and phosphorus, we have studied their reactions with mercury, silicon, tin, and bismuth aryl halides.

It was shown that treatment of phenylmercury chloride with pentaphenylantimony and -phosphorus leads to phenylation of the former. Diphenylmercury and tetraphenylantimony(-phosphorus) chloride were isolated from the reaction mixtures in yields of up to 78%.

$$Ph_5E + PhHgCl \longrightarrow Ph_2Hg + Ph_4ECl,$$
$$E = Sb, P.$$

These reactions proceed in toluene at 100°C for 1 h. Coarse crystals of tetraphenylantimony(-phosphorus) chloride are formed.

The reaction of pentaphenylantimony with ferrocenylmercury chloride under the same conditions resulted in quantitative formation of tetraphenylantimony chloride, diferrocenylmercury, and diphenylmercury. The symmetrical mercury derivatives are probably formed via intermediate formation of ferrocenyl(phenyl)mercury.

$$FcHgCl + Ph_5Sb \longrightarrow Ph_4SbCl + FcHgPh \downarrow 1/2Fc_2Hg + 1/2Ph_2Hg$$

It was previously shown that pentaarylantimony effectively arylates organotin halides [6]. We found that the reactions of pentaphenylphosphorus with tributyltin chloride and of pentaphenylantimony with tris(pentafluorophenyl)silicon bromide proceed similarly.

$$Ph_5P + Bu_3SnCl \longrightarrow Ph_4PCl + Bu_3SnPh,$$
$$Ph_5Sb + (C_6F_5)_3SiBr \longrightarrow Ph_4SbBr + (C_6F_5)_3SiPh.$$

The above reactions proceed in toluene either for 1 h at 100°C or for 24 h at room temperature. The yields of organotin and organosilicon products are 73 and 61%, respectively.

The reactions of triphenylbismuth dihalides with pentaphenylphosphorus under analogous conditions gave tetraphenylphosphorus halide, triphenylbismuth, and halobenzene. The latter products are evidently formed by decomposition of the labile tetraphenylbismuth halide.

$$Ph_5P + Ph_3BiX_2 \longrightarrow Ph_4PX + Ph_3Bi + PhX,$$
$$X = Cl, Br.$$

The resulting aryl derivatives were simiar in properties (melting points, IR spectra, TLC) to the same compounds obtained by other methods.

EXPERIMENTAL

All the reactions were carried out in evacuated glass ampules according to the following typical procedures.

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Diphenylmercury. *a*. A mixture of 2.00 g of pentaphenylantimony, 1.23 g of phenylmercury chloride, and 10 ml of toluene was heated at 100°C for 1 h. The crystals that formed were filtered off, washed with petroleum ether, and dried to obtain 1.60 g (87%) of tetraphenylantimony chloride, mp 198°C. The solvent was removed from the filtrate, and the residue was chromatographed on Silica gel L 5/40, eluent petroleum ether. Diphenylmercury, 1.10 g (78%), was obtained, mp 122°C (mp 125°C [9]).

b. A mixture of 1.00 g of pentaphenylphosphorus, 0.75 g of phenylmercury chloride, and 6 ml of toluene was kept at room temperature for 24 h. The crystals that formed were filtered off, washed with petroleum ether, and dried to obtain 0.82 g (90%) of tetraphenylphosphorus chloride. The solvent was removed from the filtrate, and the residue was chromatographed on Silica gel L 5/40, eluent petroleum ether. Diphenylmercury, 0.80 g (94%), was obtained, mp 122°C (mp 125°C [9]).

Reaction of pentaphenylantimony with ferrocenylmercury chloride. A mixture of 0.28 g of ferrocenylmercury chloride, 0.34 g of pentaphenylantimony, and 5 ml of toluene were heated at 90°C for 1 h. The crystals that formed were filtered off, washed with petroleum ether, and dried to obtain 0.30 g (96%) of tetraphenylantimony chloride. The solvent was removed from the filtrate, and the residue was chromatographed on Silica gel L 5/40, eluent petroleum ether. Diphenylmercury, 0.11 g (92%), was obtained, mp 122°C (mp 125°C [9]). The product insoluble in petroleum ether was recrystallized from toluene to obtain 0.18 g (95%) of diferrocenylmercury, mp 237°C.

Phenyltris(pentafluorophenyl)silane. A mixture of 0.60 g of tris(pentafluorophenyl)silicon bromide, 0.50 g of pentaphenylantimony, and 5 ml of toluene was heated at 100°C for 1 h. Then the reaction mixture was cooled to room temperature, and the crystals that formed were filtered off, washed with petroleum ether, and dried to obtain 0.37 g (74%) of tetraphenylantimony bromide. The solvent was removed from the filtrate, and the residue was chromatographed on alumina, eluent petroleum ether. 0.37 g (61%) of crystals were obtained, mp 48°C.

Tributylphenyltin. A mixture of 1.00 g of pentaphenylphosphorus, 0.78 g of tributyltin chloride, and 6 ml of toluene was kept at room temperature for 24 h. The crystals that formed were filtered, washed with petroleum ether, and dried to obtain 0.71 g (79%) of tetraphenylphosphorus chloride. The solvent was removed from the filtrate, and the residue was chromatographed on Silica gel L 5/40, eluent petroleum ether. Tributylphenyltin, 0.64 g (73%) was obtained.

Reaction of pentaphenylphosphorus with triphenylbismuth dichloride. A mixture of 0.50 g of pentaphenylphosphorus, 0.61 g of triphenylbismuth dichloride, and 30 ml of toluene was heated at 100°C for 1 h. The reaction mixture was cooled, the solvent was removed, and the residue was treated with petroleum ether (3×50 ml). The substance insoluble in petroleum ether was tetraphenylphosphorus chloride, 0.40 g (89%), mp 262°C. The ethereal extracts were evaporated to isolate 0.52 g (98%) of triphenylbismuth, mp 72°C.

Reaction of pentaphenylphosphorus with triphenylbismuth difluoride was performed in a similar way. Tetraphenylphosphorus bromide (84%) and triphenylbismuth (96%) were isolated.

Reaction of pentaphenylphosphorus with triphenylbismuth difluoride was performed in a similar way. Tetraphenylphosphorus fluoride (98%) and triphenylbismuth (96%) were isolated.

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