Dr. W. C. Wildman for this appointment. The author wishes to thank particularly Dr. Wildman and Dr. H. C. Fales for stimulating discussions and helpful suggestions.

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Reaction of Triphenyltin Hydride with Some Organic Halides and Amines

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Received May 15, 1961

The ability of triphenyltin hydride to convert organic halides and amines to the corresponding hydrocarbon and triphenyltin halide and hexaphenylditin, respectively, is a relatively new development in organotin chemistry.[1,2] In connection with a study of the stereochemistry of these reactions currently being carried out in these laboratories, it was necessary to see if triphenyltin hydride would satisfactorily react with *dl-α*-phenethyl chloride and *dl-α*-methylbenzylamine. It was also considered of interest to study the reaction of triphenyltin hydride with benzyl chloride and benzylamine.

The experimental procedure employed was similar to that reported for the reaction of triphenyltin hydride with allyl bromide and allylamine.[3] The reaction of triphenyltin hydride with benzyl chloride gave triphenyltin chloride (65.6%) and toluene (25.5%). With *dl-α*-phenethyl chloride there was obtained triphenyltin chloride (68.4%) and ethylbenzene (79.4%).

The reaction of triphenyltin hydride with benzylamine in the molar ratio of 2:1 gave hexaphenylditin (75.8%), toluene, and ammonia. With *dl-α*-methylbenzylamine there was obtained hexaphenylditin (52.7%) and ammonia.

The liquid products were isolated by distillation of the reaction mixture and were identified by the fact that their infrared spectra were superimposable upon those of authentic samples. No attempt was made to separate quantitatively the liquid product from the solid. In the case of benzylamine the mixture was distilled only until enough of the liquid was obtained for an infrared spectral determination. In the case of *dl-α*-methylbenzylamine, ethylbenzene was probably formed, but it was not isolated. In this reaction an amount of unchanged *dl-α*-methylbenzylamine was isolated which was consistent with the yield of hexaphenylditin. The solids were isolated as quantitatively as possible and were identified by the fact that admixture with authentic samples did not depress the melting points.

In each of the above reactions a small quantity of tetraphenyltin was isolated. This compound may have been formed from unchanged triphenyltin hydride during processing of the reaction mixture. It is reported that triphenyltin hydride is decomposed by air and by exposure to light with separation of tetraphenyltin.[4]

EXPERIMENTAL

Melting points were determined in open capillaries and are uncorrected. All the reactions were carried out in a nitrogen atmosphere.[5]

Reaction of triphenyltin hydride with benzyl chloride. Triphenyltin hydride[4] (30.0 g., 0.0854 mole) was added to a dry 50-ml. flask fitted with a Claisen head, thermometer, and condenser. Freshly distilled benzyl chloride (10.8 g., 0.0854 mole), b.p. 176°, was added in one portion, and the system was evacuated. The reaction mixture was placed under 1 atm. of nitrogen and then was heated with occasional shaking at 80° ± 5° for 4 hr. After 4 hr. a colorless crystalline material was evident in the reaction mixture.

The mixture was distilled at atmospheric pressure (pot temperature to 140°). The distillation was stopped when the residue began to turn brown. There was obtained 2.0 g. (25.5%) of toluene, b.p. 109–110°, infrared spectrum superimposable upon that of an authentic sample of toluene.

The brown residue was refluxed with two 25-ml. portions of diethyl ether, and the cloudy solution was filtered. The ether-insoluble material, m.p. 223–225°, weighed 1.5 g. Admixture with an authentic sample of tetraphenyltin did not depress the melting point. There was no metallic tin mixed with the product.

The ether solution was evaporated to dryness, and the crude product was recrystallized from ethanol. There was obtained 21.6 g. (65.6%) of triphenyltin chloride, m.p. 105–106°, melting point undepressed on admixture with an authentic sample of triphenyltin chloride.

Reaction of triphenyltin hydride with dl-α-phenethyl chloride. Triphenyltin hydride[4] (30.0 g., 0.0854 mole) was placed in a dry, 50-ml. flask equipped with a Claisen head, thermometer, and condenser. *dl-α*-Phenethyl chloride[6] (12.0 g., 0.0854 mole), b.p. 77–78° (17.5 mm.) [lit.[6,7] b.p. 78–82° (17 mm.), 74–75° (14 mm.)] was added in one portion, and the system was evacuated. The reaction mixture was placed under 1 atm. of nitrogen and heated to 80° ± 5°. After 1 hr. the temperature suddenly rose from 80° to 140°. The temperature rise was accompanied by heavy refluxing. The mixture was cooled to 40°, and when it failed to solidify, it was heated to 80° ± 5°. The mixture was maintained at this temperature, with occasional shaking, for 7 hr.

The mixture was distilled (pot temperature to 140°). The colorless distillate, b.p. 128° to 133°, weighed 7.2 g., and was redistilled. The fraction boiling at 131° to 133° was collected. The infrared spectrum of this material was superimposable upon that of an authentic sample of ethylbenzene, b.p. 134–136°.

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(5) For a description of the apparatus, see W. S. Johnson and G. H. Daub, *Org. Reactions*, **6**, 43 (1951).

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The solid residue from the distillation was refluxed with two 25-ml. portions of diethyl ether, and the cloudy solution was filtered. There was obtained 2.7 g. of a mixture of products. Metallic tin was physically separated from the white powder which was identified as tetraphenyltin by the fact that admixture with an authentic sample of tetraphenyltin did not depress the melting point.

The ether was evaporated, and the crude product was recrystallized from ethanol. There was obtained 22.5 g. (68.4%) of triphenyltin chloride, m.p. 104–105°, melting point undepressed on admixture with an authentic sample of triphenyltin chloride.

Reaction of triphenyltin hydride with benzylamine. Triphenyltin hydride[4] (60.0 g., 0.1708 mole) was placed in a dry 250-ml. flask fitted with a Claisen head, truebore-stirrer, and condenser. Freshly distilled benzylamine (9.15 g., 0.0854 mole), b.p. 77.5–78° (19 mm.), was added in one portion, and the system was evacuated. The mixture was stirred at room temperature under 1 atm. of nitrogen for 24 hr.

During the course of the reaction the system was evacuated often to remove the ammonia vapors, but was always returned to the original 1 atm. of nitrogen. After 11 hr., the first indications of solid materials became evident. At the end of 24 hr. the reaction mixture had become a thick white paste. The ammonia vapors were taken off *in vacuo*, and the mixture was heated to 80° ± 5° until there was no further evidence of ammonia being evolved. This required about 2.5 hr. The temperature was reduced to 65°, and the mixture was distilled under slight vacuum. The infrared spectrum of the distillate was superimposable upon that of an authentic sample of toluene.

The gray-black residue was refluxed with seven 150-ml. portions of diethyl ether and filtered. Evaporation of the ether gave 1.5 g. of a yellow powder, m.p. 140–150°. Repeated recrystallization from benzene yielded a white powder, m.p. 223–225°, melting point undepressed on admixture with an authentic sample of tetraphenyltin.

The granular residue from the ether extractions was recrystallized from benzene. There was obtained 45.3 g. (75.8%) of hexaphenylditin, m.p. 237–238°, melting point undepressed on admixture with an authentic sample of hexaphenylditin.

Reaction of triphenyltin hydride with dl-α-methylbenzylamine. Run No. 1. Triphenyltin hydride[4] (15.0 g., 0.0427 mole) was added to a dry 100-ml. flask fitted with a true bore-stirrer and condenser. *dl*-α-Methylbenzylamine (2.6 g., 0.0214 mole) was added in one portion, and the mixture was heated to 80° ± 5° under a running stream of nitrogen with stirring.

After 8 hr. the thick paste was dissolved in benzene, and the solution was allowed to remain in the refrigerator overnight. The solution was evaporated to one fourth its original volume and refrigerated again. The yellow granular material which crystallized was recrystallized twice from benzene. There was obtained 5.0 g. (34%) of hexaphenylditin, m.p. 229–230°, melting point undepressed on admixture with an authentic sample of hexaphenylditin.

Run No. 2. Triphenyltin hydride[4] (60.0 g., 0.1708 mole) was placed in a dry 250-ml. flask equipped with a Claisen head, truebore-stirrer, and condenser. *dl*-α-Methylbenzylamine (10.34 g., 0.0854 mole) was added in one portion, and the system was evacuated. The mixture was stirred at room temperature under 1 atm. of nitrogen for 24 hr.

During the course of the reaction the system was evacuated often to remove the ammonia vapors. The system was always returned to the original 1 atm. of nitrogen. After 24 hr. the pasty white mixture was heated to 80° ± 5° until there was no further evidence of ammonia being evolved. This required about 2.5 hr. The mixture was vacuum distilled (pot temperature to 85°). The colorless distillate, b.p. 71–75° (*ca.* 20 mm.), weighed 5.0 g. The infrared spectrum of the distillate was superimposable upon that of *dl*-α-methylbenzylamine. Careful redistillation of the distillate failed to yield any ethylbenzene.

The residue was refluxed with seven 150-ml. portions of diethyl ether. Evaporation of the ether gave 1.3 g. of a light tan powdery solid. Repeated recrystallization from benzene yielded a white powder, m.p. 223–225°, melting point undepressed on admixture with an authentic sample of tetraphenyltin.

The granular residue from the ether extractions was recrystallized from benzene. There was obtained 31.5 g. (52.7%) of hexaphenylditin, m.p. 234–236°, melting point undepressed on admixture with an authentic sample of hexaphenylditin.

Further processing of the mother liquor yielded 6.5 g. of a fluffy white solid, m.p. 295–300°. Repeated recrystallization from benzene-ethanol gave 2.0 g. of a white solid, m.p. 304–307°. This material was not identified. The infrared spectrum was essentially identical to those of tetraphenyltin and hexaphenylditin.

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Attempted Polymerization of 2-Substituted Tetrahydrofurans

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Received May 15, 1961

Although the polymerization of tetrahydrofuran by Lewis-type acids is well known, very little has been published on the ring opening and polymerization of tetrahydrofurans substituted at the 2-position.

We have found that 2-methyltetrahydrofuran and 2,5-dimethyltetrahydrofuran do not polymerize under conditions which readily polymerize tetrahydrofuran (Table I).

In all runs with the substituted compounds, no diol was obtained on workup but instead almost 100% recovery of starting material was realized.

Polymerization of a mixture of equal weights of tetrahydrofuran and 2-methyltetrahydrofuran yielded only the homopolymer of the former. 98% of the latter compound was recovered unchanged. The catalyst employed in this experiment was antimony pentachloride (10% total weight of both compounds).

The polymerizability of tetrahydrofuran to the polytetramethyleneglycol and the inability to obtain the branched chain polyglycol from the 2- or 2,5- derivatives is more likely a question of the steric conditions associated with the attack of a ring-opened structure on a second molecule rather than the ability to form the coordinate compound of the ring and metal. Thus, it was observed that for all compounds, heat was generated when catalyst was added to the reaction medium regardless of the substitution on the furan ring. Table II describes the change in temperature of the reaction