

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

Some Reactions of Tetra-*para*-tolytin

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The reactions of tetraphenyltin have been reported by Bost and Borgstrom,¹ Smith and Kipping² have studied the reaction of tetra-*p*-tolytin with two moles of bromine, whereupon ditolylstannic dibromide was obtained.

This work was undertaken to determine whether tetra-*p*-tolytin could be used to prepare *para* substitution products of toluene free from the *ortho* isomers and also whether the side chain entered into any of these reactions. The formation of pure *p*-nitrotoluene is noteworthy in this connection. Since the substitution of a methyl group in the benzene ring enhances the activity of the ring, tetra-*p*-tolytin should be very reactive toward entering substituents. Its action with iodine bears out this prediction. Tetraphenyltin does not react appreciably under similar conditions. Other reagents also show this difference in reactivity, although less pronounced. In this work tetra-*p*-tolytin was studied with the halogens, alkyl halides, acyl halides, mineral acids and sulfur.

The tetra-*p*-tolytin was prepared by the action of stannic bromide on *p*-tolylmagnesium bromide in 52% yields. Pfeiffer³ who first prepared it obtained only a 24.8% yield. It is a white crystalline substance melting at 230°.

Action of Halogens

Chlorine.—To 9.66 g. of tetra-*p*-tolytin in a 250-ml. flask cooled in ice and attached to a reflux condenser, was slowly added a cold solution of 5.68 g. of chlorine in 150 ml. of chloroform. After refluxing for one hour on a steam-bath, the solvent was removed by distillation. The residue was transferred to a small flask and distilled. An 85% yield of *p*-chlorotoluene was obtained, b. p. 162–163°, m. p. 7°. No isomeric products were obtained. The reaction was repeated at room temperature and also in boiling carbon tetrachloride. In all cases only *p*-chlorotoluene was obtained.

Bromine.—The above experiment was repeated using 9.66 g. of tetra-*p*-tolytin and adding 12.78 g. of bromine dropwise. Much heat was evolved with the formation of a colorless liquid. After gently refluxing for an hour a 90% yield of *p*-bromotoluene was obtained upon distillation, b. p. 184–185°, m. p. 28°. No isomers were obtained.

Iodine.—To 9.66 g. of tetra-*p*-tolytin in a 500-ml. flask was added slowly a cold solution of 20.3 g. of iodine in carbon tetrachloride. The iodine solution was decolorized as fast as added until about one-half had been added. After refluxing for an hour, the solvent was removed and finally the *p*-iodotoluene; yield 81%, b. p. 210–211°, m. p. 35°. No isomers were obtained.

Action of Alkyl Halides

Tetra-*p*-tolytin in 0.02-mole portions was heated under reflux for thirty-six hours

(1) Bost and Borgstrom, *THIS JOURNAL*, **51**, 1922 (1929).

(2) Smith and Kipping, *J. Chem. Soc.*, **103**, 2049 (1913).

(3) Pfeiffer, *Z. anorg. Chem.*, **68**, 104 (1910).

with a slight excess of ethyl and isopropyl bromides, respectively. No reaction occurred and the products were recovered unchanged.

Tert-butyl Bromide.—9.66 g. of tetra-*p*-tolyltin was refluxed for eighteen hours with 10.96 g. of *tert*-butyl bromide. The products of reaction consisted of some unused tetra-*p*-tolyltin, hydrogen bromide, isobutylene, traces of toluene and some unused halide.

Action of Acyl Halides

Acetyl Chloride.—9.66 g. of tetra-*p*-tolyltin was refluxed on a steam-bath with 6.28 g. of acetyl chloride for twenty-four hours. A reaction occurred but no definite substance could be identified. No methyl tolyl ketone was obtained.

Benzoyl Chloride.—9.66 g. of tetra-*p*-tolyltin and 11.24 g. of benzoyl chloride were refluxed for six hours on a steam-bath. The cold product was extracted with dilute sodium hydroxide to remove any benzoic acid. The mass was extracted with ether, which yielded a tarry residue upon evaporation. When the residue was recrystallized from petroleum ether, a 5% yield of *p*-tolyl phenyl ketone was obtained, m. p. 59°.

Benzene Sulfonyl Chloride.—9.66 g. of tetra-*p*-tolyltin and 7.5 g. of benzene sulfonyl chloride were heated in a sealed tube at 200° for five hours. The product was extracted with benzene, which yielded a dark residue. The latter was recrystallized from acetone. An 84.3% yield of *p*-tolyl phenyl sulfone was obtained, m. p. 124°. No definite product could be isolated when the reaction was carried out under reflux for twenty-four hours.

Action of Acids

Nitric Acid.—To 9.66 g. of tetra-*p*-tolyltin in a flask surrounded by ice and attached to a reflux condenser was added dropwise 5 ml. of concentrated nitric acid. A violent action soon occurred, evolving much heat. After the reaction had subsided, the mixture was heated on a steam-bath for thirty minutes, the product washed with water, and extracted with hot alcohol. The residue from the alcohol extract was recrystallized from dilute alcohol. Long pale yellow needles of *p*-nitrotoluene separated, yield 85%, m. p. 55°. No ortho isomer was found in the reaction.

Sulfuric Acid.—The above experiment was repeated using concentrated sulfuric acid instead of nitric acid. A vigorous reaction occurred. The mixture was heated on a steam-bath for one hour and distilled. A 94% yield of toluene was obtained, b. p. 110–111°. A similar yield was obtained at room temperature.

Action of Sulfur

***p*-Ditolyl Disulfide.**—9.66 g. of tetra-*p*-tolyltin and 1.92 g. of sulfur (three equivalents) were heated at 170° in a sealed tube for ten hours. The reaction product was extracted with ether. A light brown oil was obtained which gave a 45% yield of *p*-ditolyl disulfide upon distillation, b. p. 298–300°, m. p. 44–5°.

3,7-Dimethylthianthrene.—The reaction was repeated using five equivalents of sulfur and heating the tube at 190° for eight hours. The extract gave a product which upon purification gave an 80% yield of 3,7-dimethylthianthrene, m. p. 123°.

Summary

Tetra-*p*-tolyltin reacts with halogens to form the corresponding aryl halides, with nitric and sulfuric acids to form *p*-nitrotoluene and toluene, respectively, and with sulfur under different conditions to form *p*-ditolyl disulfide and 3,7-dimethylthianthrene. No isomers were obtained with the halogens or nitric acid. Reactions of acyl and alkyl halides are less marked.