2. The uronic acid has not been obtained in crystalline condition. It may be oxidized to a dibasic C_6 sugar acid. The diamide and diphenylhydrazide of this acid correspond in properties to the analogous compounds prepared from pure *d*-mannosaccharic dilactone.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

TIN TETRAPHENYL AS A PHENYLATING REAGENT

BY R. W. BOST AND P. BORGSTROM

RECEIVED FEBRUARY 25, 1929 PUBLISHED JUNE 5, 1929

Certain of the organo-metallic compounds have been used as phenylating reagents. Mercury[1] and magnesium diphenyl[2] have been used to introduce the phenyl groups into certain compounds. Aryl tin halides were first made by the reaction of mercury diphenyl and stannic chloride.[3] Later the reaction between tin tetraphenyl and halogens to form mono-, di and triaryl halides has been carefully studied.[4] More recently Goddard and his co-workers[5] have isolated products from tin tetraphenyl and thallic chloride, while no derivatives were obtainable with the chlorides of mercury and sulfur with tin tetraphenyl.

Since tin tetraphenyl is comparatively rich in phenyl groups, and since its toxicity is much lower than that of mercury diphenyl, it seemed desirable to study the possibilities of using it as a reagent for introducing the phenyl group into organic compounds. In this paper are presented the reactions of tin tetraphenyl with the following types of compounds: halogens, alkyl halides, acyl halides, sulfur, nitric acid and sulfuryl chloride.

Experimental Part

1. Action of Halogens.—Bromine and chlorine react violently with tin tetraphenyl. Even at 0° they react energetically to give excellent yields of the corresponding monohalides of benzene. The reaction using iodine is less active and low yields of phenyl iodide are obtained. Iodine monochloride reacts very readily and produces a good yield of phenyl iodide. No halogen disubstitution products of benzene were detected under the conditions of the experiment.

Bromobenzene.—Twelve and seven-tenths grams of bromine was slowly added with a dropping funnel to 8.5 g. of tin tetraphenyl in a round-bottomed flask connected with a reflux condenser, the flask being cooled in an ice–salt mixture. The bromine was rapidly taken up, forming a colorless liquid, until most of the bromine had been

---

[1] Dreher and Otto, *Ann.*, **154**, 97 (1870).

[2] Waga, *ibid.*, **282**, 323 (1894).

[3] Aronheim, *ibid.*, **194**, 145 (1878).

[4] Polis, *Ber.*, **22**, 2918 (1899); Krause, *ibid.*, 51, 912 (1918); Chambers and Scherer, THIS JOURNAL, **48**, 1055 (1926).

[5] Goddard and Goddard, *J. Chem. Soc.*, **121**, 256 (1922); Goddard, Ashley and Evans, *ibid.*, **121**, 978 (1922).

added. Much heat was evolved in the reaction. After all of the bromine had been added, the reaction mixture was heated on a steam-bath for one hour. The phenyl bromide was removed by distillation, then washed, dried and redistilled. The fraction boiling from 154–156° was collected; yield, 94%.

Chlorobenzene.—To 8.5 g. of tin tetraphenyl in a cooled flask as above described was slowly added 5.7 g. of chlorine dissolved in carbon tetrachloride. A vigorous reaction took place, evolving much heat. After all of the chlorine had been added, the mixture was heated for thirty minutes on the steam-bath. The chlorobenzene was distilled off, washed, dried and the fraction boiling between 131–133° was reserved; yield, 91%.

Iodobenzene.—An apparatus similar to the one in the above experiments was used; 13 g. of iodine monochloride dissolved in 200 ml. of carbon tetrachloride was slowly added to 8.5 g. of tin tetraphenyl in a flask cooled with ice. The addition required about twenty minutes. The mixture was refluxed for four hours and set aside for twenty-four hours. The carbon tetrachloride was distilled from the steam-bath, and then the crude iodobenzene. The phenyl iodide was washed, dried and the fraction 187–188° reserved; yield, 74%.

2. Action of Alkyl Halides.—Certain alkyl halides were heated with tin tetraphenyl but poor results were obtained with this group of compounds. There seems to be a tendency for the alkyl halides to split off halogen acids, giving an unsaturated hydrocarbon, the triaryl tin halide and some unused tin tetraphenyl. This is true with *iso*-amyl bromide and to a certain extent with *tert.*-butyl bromide. Chloroform and bromoform gave no apparent reaction under ordinary conditions. The former in a sealed tube gave mostly triphenyl tin chloride.

***Tert.*-Butylbenzene.**—A mixture of 8.5 g. of tin tetraphenyl and 12 g. of *tert.*-butyl bromide was heated under reflux for eighteen hours. As the reaction proceeded the solution after first darkening became light in color. The reaction product was filtered, excess of *tert.*-butyl bromide distilled off and the *tert.*-butylbenzene distilled under reduced pressure; yield, 8%. An unsaturated hydrocarbon, a halogen acid and the aryl tin halide were also formed.

Reaction with *Iso*-amyl Bromide.—Eight and five-tenths grams of tin tetraphenyl and 13 g. of *iso*-amyl bromide were refluxed for twenty hours. The reaction product gradually darkened. The presence of a halogen acid, an unsaturated hydrocarbon and the aryl tin halide were detected but the main product was unchanged tin tetraphenyl and *iso*-amyl bromide. No *iso*-amylbenzene was observed.

Reaction with Chloroform.—Twelve and seven-tenths grams of tin tetraphenyl and 4.7 g. of chloroform were heated in a sealed tube at 260° for twenty hours. The brownish-yellow residue was washed from the tube with ether and filtered. The insoluble portion consisted mainly of unused tin tetraphenyl. The filtrate after being decolorized with charcoal yielded three grams of triphenyl tin chloride and traces of triphenylmethane.

3. Action of Acyl Halides.—The reaction between tin tetraphenyl and acetyl chloride, benzoyl chloride, and benzene sulfonyl chloride to form ketones was very slow under ordinary conditions. Only traces of phenyl ketones were obtained when boiled under reflux. High temperatures and pressures were necessary to produce an appreciable yield and even then the yield was poor in the case of acetyl chloride.

Acetophenone.—Eight and five-tenths g. of tin tetraphenyl and 10 g. of acetyl chloride were heated in a sealed tube at 100° for fifteen hours. A dark oil was obtained. This was filtered and the filtrate was washed, dried and distilled. After two fractionations a light yellow oil was obtained which boiled at 200–205°; yield of acetophenone, 1 g.

Benzophenone.—Eight and five-tenths g. of tin tetraphenyl and 12.5 g. of benzoyl chloride were heated in a sealed tube at 200° for ten hours. The reaction product was washed from the tube with ether and filtered. The ether was evaporated and the brownish oil repeatedly washed with hot water to destroy any unused benzoyl chloride. The brownish liquid partially solidified. It was transferred to a distilling flask and the portion coming over from 297 to 305° was reserved; crude yield, 7%; redistilled and recrystallized from alcohol, m. p. 48°.

Diphenylsulfone.—Eight and five-tenths g. of tin tetraphenyl and 14.1 g. of benzenesulfonyl chloride were heated in a sealed tube at 200° for eighteen hours. The dark viscous product in the tube was rinsed out with benzene and filtered. The filtrate yielded 34% of crude diphenylsulfone. The crude product was purified from hot water; m. p. 122–124°.

4. Action of Sulfur.—Reactions between tin tetraphenyl and sulfur were carried out under different conditions of time, temperature and concentrations of sulfur. As the temperature was increased the products changed from diphenyl sulfide to diphenyl disulfide and to thianthrene, using more sulfur for the second and third than for the first. It is necessary to carry out the reactions in a sealed tube to get the best results.

Diphenyl Sulfide.—Eight and five-tenths g. of tin tetraphenyl and 1.9 g. of flowers of sulfur (three atomic weights) were heated in a sealed tube at 170° for ten hours. The reaction product was a golden yellow liquid. The product was filtered and distilled. About two grams of benzene was obtained as a by-product. The diphenyl sulfide boiled at 295–297°; yield, 76%.

Diphenyl Disulfide.—Eight and five-tenths g. of tin tetraphenyl and 3.2 g. (five atomic weights) of sulfur were heated in a sealed tube at 190° for eight hours. The reaction product consisted of a brownish-yellow solid. This was extracted with hot ether, which upon evaporation and distillation yielded two grams of diphenyl sulfide and 4.8 g. of diphenyl disulfide (m. p. 60°).

Thianthrene.—Eight and five-tenths g. of tin tetraphenyl and 3.2 g. (five atomic weights) of sulfur were heated in a sealed tube at 250° for twenty hours. Hydrogen sulfide was given off when the tube was opened. The brownish-yellow product was extracted with ether and filtered. It was only slightly soluble in ether. It was then extracted with hot absolute alcohol and filtered. From the filtrates were isolated 2 g. of phenyl sulfide, less than 1 g. of diphenyl disulfide and about 2 g. of thianthrene (m. p. 155–158°).[6]

5. Action with Nitric Acid.—To 8.5 g. of tin tetraphenyl in a flask cooled with an ice–salt mixture and fitted with a reflux condenser, was slowly added 5 ml. of concentrated nitric acid. At first only a gentle reaction occurred. Soon a violent reaction was set up. After the reaction had ceased the product was heated on a steam-bath for thirty minutes. The product was then washed, dried and distilled. The fraction boiling at 208–210° was reserved; yield, 2 g. Whether the nitrobenzene was formed when the tin tetraphenyl was decomposed or whether benzene was first formed and then nitrated is not known from these experiments.

6. Action of Sulfuryl Chloride.—From the product of refluxing 8.5 g. of tin tetraphenyl with 5.4 g. of sulfuryl chloride in benzene were isolated only unchanged tin tetraphenyl and a small amount of triphenyl tin chloride (m. p. 105–106°). When 8.5 g. of tin tetraphenyl and 20 ml. of sulfuryl chloride (without solvent) were refluxed, sulfur dioxide was evolved and only a small amount of diphenyl tin hydroxychloride (m. p. 184–185°) was identified. What the course of this reaction is and what other products are formed need further study.

---

[6] In all cases the compound isolated whose melting point or boiling point is given was checked by mixing with the same compound from another source and again determining the constant.

Summary

1. Tin tetraphenyl reacts with (*a*) halogens to form aryl mono halides, (*b*) acyl halides to form phenyl ketones, (*c*) sulfur to form diphenyl sulfide, diphenyl disulfide and thianthrene. The reactions with alkyl halides and sulfuryl chloride were not conclusive. With nitric acid nitrobenzene was isolated.

Chapel Hill, North Carolina
Washington, D. C.

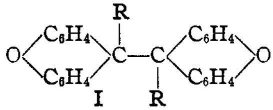
[Contribution from the Chemical Laboratory of Harvard University]

THE DISSOCIATION INTO FREE RADICALS OF SUBSTITUTED DIXANTHYLS. V. THE RATE OF DISSOCIATION[1]

By James B. Conant and Mildred W. Evans[1]

Received February 28, 1929 Published June 5, 1929

More than a dozen derivatives of dixanthyl of the type represented by Formula I have been prepared and studied in this Laboratory.[2]



$$O\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\overset{R}{C}-\underset{R}{C}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}O$$

I

(R = an alkyl or aryl group)

All of them in solution absorb oxygen at room temperature and in many cases the reaction is so rapid that the speed of the process is limited only by the rate of solution of the gas. However, those compounds in which the substituting group may be represented as RCH_2CH_2— are much less rapid in their action and it is possible, therefore, to study their auto-oxidation at room temperature. A few approximate measurements of the rate of oxidation of these substances were made in connection with their preparation; these results have been reported in the previous papers of this series. In order to learn more about the nature of the reaction, we have now undertaken a more detailed study of the auto-oxidation of a typical representative of the class, di-*n*-butyldixanthyl. The results of this investigation, which we are about to describe, led to the unexpected conclusion that we were in reality measuring a rate of dissociation into free radicals. Since the relation between this rate and the tendency of the compound to dissociate on heating is a matter of great interest, we continued the work and included a study of a number of homologs of di-*n*-butyldixanthyl at different temperatures. A discussion of the results so obtained forms the concluding portion of this paper.

In the case of many compounds which are appreciably dissociated in

---

[1] This paper is part of a thesis presented by Mildred W. Evans at Radcliffe College for the degree of Doctor of Philosophy.

[2] Conant and co-workers, This Journal, **47,** 572, 3068 (1925); **48,** 1743 (1926); **49,** 2080 (1927).