[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOBART COLLEGE]

A SERIES ARRANGEMENT OF ORGANIC GROUPS. I. AS DETERMINED BY THE HALOGENATION OF MIXED STANNANES

BY RALPH H. BULLARD

RECEIVED MAY 14, 1929 PUBLISHED OCTOBER 5, 1929

When a tetra-alkyl- or arylstannane is treated with two atoms of halogen one of the organic groups is replaced by halogen. The reaction is represented by the equation $R_4Sn + X_2 = R_3SnX + RX$. When a mixed alkyl- or alkylarylstannane such as R_3SnR' is halogenated, two reactions are possible

$$R_3SnR' + X_2 = R_3SnX + R'X \quad (1)$$
$$R_3SnR' + X_2 = R_2R'SnX + RX \quad (2)$$

It is a remarkable fact that in general only one of these reactions occurs. We may consider, therefore, that the velocity of one reaction is enormously greater than that of the other, or that the affinities of the groups are such that only one reaction occurs. In any case, the groups can be arranged in a series corresponding with the order of their removal by means of halogen.

Grüttner and Krause[1] from their investigations of mixed alkylplumbanes formulated a rule stating that, on bromination, the lightest group splits off first. Later, on working with mixed alkylstannanes, these authors state[2] that, without exception, the same rule applies to the alkylstannanes.

Frankland[3] and also Morganoff[4] state that, on iodination of dimethyldiethylstannane, $(CH_3)_2(C_2H_5)_2Sn$, the methyl group is removed before the ethyl. Pope and Peachey[5] found that on iodinating trimethylethylstannane, $(CH_3)_3C_2H_5Sn$, and dimethylethylpropylstannane, $(CH_3)_2(C_2H_5)(C_3H_7)Sn$, the methyl group is in each case removed first. Cahours,[6] however, reports that an ethyl group is removed on iodinating trimethylethylstannane. Bullard and Vingee[7] found that trimethylethylstannane, on bromination, yields dimethylethylstannyl bromide, $(CH_3)_2(C_2H_5)SnBr$, with the removal of a methyl group. This does not agree with the observations of Cahours but is in accord with those of Frankland, Morganoff and Pope and Peachey.

Ladenburg[8] found that iodination of triethylphenylstannane, $(C_2H_5)_3(C_6H_5)Sn$, yields iodobenzene and triethylstannyl iodide, $(C_2H_5)_3SnI$, while

---

[1] Grüttner and Krause, *Ber.*, **50**, 202 (1917).

[2] Grüttner and Krause, *ibid.*, **50**, 1802 (1917).

[3] Frankland, *Ann.*, **111**, 44 (1859).

[4] Morganoff, *ibid.*, **144**, 157 (1867).

[5] Pope and Peachey, *Proc. Chem. Soc.*, **16**, 42 (1900).

[6] Cahours, *Ann.*, **122**, 49 (1862).

[7] Bullard and Vingee, THIS JOURNAL, **51**, 892 (1929).

[8] Ladenburg, (a) *Ber.*, **4**, 17 (1871); (b) *Ann.*, **159**, 251 (1871).

Krause and Schmitz[9] showed that the phenyl group is removed before ethyl with such reagents as silver nitrate or mercuric chloride. Bullard and Robinson[10] found that on bromination of trimethylphenylstannane, $(CH_3)_3(C_6H_5)Sn$, the phenyl group is removed.

It has been shown by Kipping and Smith[11] that the benzyl group is removed before ethyl by iodine, sulfuric acid or chlorosulfuric acid. Kraus and Bullard[12] showed that the benzyl group is removed on brominating trimethylbenzylstannane, $(CH_3)_3(C_6H_5CH_2)Sn$.

In the experimental part of this paper it is shown that the phenyl group is removed before the benzyl group.

From the above it is seen that the series of groups arranged in the order of decreasing ease of removal from tin by free halogen is as follows: phenyl, benzyl, methyl, ethyl, propyl.

In a later paper the author hopes to present the order of substitution for mixed stannanes of the type $R_2SnR'_2$ when treated with halogen acids.

Experimental Part

Preparation of Triphenylbenzylstannane, $(C_6H_5)_3(C_6H_5CH_2)Sn$.—Triphenylstannyl iodide was dissolved in liquid ammonia and converted into the sodium salt by adding two atoms of sodium per mole of iodide. The theoretical amount of benzyl chloride was then added. A white precipitate was formed. The reaction took place according to the equation $NaSn(C_6H_5)_3 + C_6H_5CH_2Cl = (C_6H_5)_3(C_6H_5CH_2)Sn + NaCl$. The ammonia was allowed to evaporate and water was added to dissolve the sodium chloride. The residual white powder was dried and crystallized from petroleum ether; yield, practically quantitative. The substance melted at 90–91°.

Anal. Subs., 0.2579, 0.2584: SnO_2, 0.0873, 0.0880. Calcd. for $(C_6H_5)_3(C_6H_5CH_2)Sn$: Sn, 26.94. Found: Sn, 26.66, 26.82.

Mol. wt. Subs., 0.3095, 0.4317: C_6H_6, 19.25, 19.25; Δt, 0.189, 0.267. Calcd. for $(C_6H_5)_3(C_6H_5CH_2)Sn$: mol. wt., 440.7. Found: mol. wt., 435.7, 426.8.

Bromination of Triphenylbenzylstannane.—The stannane was brominated by adding to its benzene solution cooled in ice water a carbon tetrachloride solution of four atoms of bromine per mole of stannane. Bromination took place instantly. The benzene and carbon tetrachloride were removed by distillation from a steam-bath under atmospheric pressure. The pressure was then reduced and a liquid was obtained which boiled under atmospheric pressure at 154° uncorr. This indicated the presence of bromobenzene. The residual liquid did not distil at 100° under a pressure of three millimeters. On cooling it solidified and was crystallized from petroleum ether. Large colorless prisms melting at 74–75° were obtained. This further indicated that phenyl groups had been removed with the formation of phenylbenzylstannyl dibromide because diphenylstannyl dibromide melts at 36–38°.

Anal. Subs., 0.1024, 0.1581: SnO_2, 0.0408, 0.0536. Calcd. for $(C_6H_5)(C_6H_5CH_2)SnBr_2$: Sn, 26.59. Found: Sn, 26.69, 26.70. Subs., 0.1669, 0.2503: AgBr, 0.1391, 0.2099. Calcd. for $(C_6H_5)(C_6H_5CH_2)SnBr_2$: Br, 35.79. Found: Br, 35.47, 35.69.

---

[9] Krause and Schmitz, *Ber.*, **52,** 2150 (1919).

[10] Bullard and Robinson, THIS JOURNAL, **49,** 1372 (1927).

[11] Kipping and Smith, *J. Chem. Soc.*, **101,** 2552 (1912).

[12] Kraus and Bullard, THIS JOURNAL, **48,** 2135 (1926).

Hence the bromination of triphenylbenzylstannane results in the removal of phenyl groups, the reaction proceeding according to the equation $(C_6H_5)_3(C_6H_5CH_2)Sn + 2Br_2 = (C_6H_5)(C_6H_5CH_2)SnBr_2 + 2C_6H_5Br$.

The author wishes to acknowledge his indebtedness to the Warren Fund of the American Academy of Arts and Sciences for a grant which assisted in defraying the expenses of the present investigation.

Summary

1. It has been shown that on bromination of triphenylbenzylstannane the phenyl groups are first removed.

2. The series arrangement of some organic groups based on the relative ease of removal from tin by halogen is: phenyl, benzyl, methyl, ethyl, propyl.

GENEVA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

THE CONSTITUTION OF TRIPHENYLSILICANE AND ITS REACTION WITH SODIUM IN LIQUID AMMONIA[1]

BY HARRY H. REYNOLDS,[2] LUCIUS A. BIGELOW AND CHARLES A. KRAUS

RECEIVED MAY 18, 1929 PUBLISHED OCTOBER 5, 1929

The present study was undertaken as a part of a broader investigation now in progress in this Laboratory, which deals with certain of the fundamental properties of the element silicon in its organic combinations. In attacking this problem it was necessary to form organic silicon derivatives of the general type R_3SiNa to be used as reagents. Since the corresponding halides R_3SiX are completely ammonolyzed by liquid ammonia, it was attempted to prepare the desired compound by the action of sodium on triphenylsilicane in the same solvent. The corresponding reaction of sodium with triphenylstannane takes place readily and quantitatively. When, however, this simple reaction was attempted in the case of the silicane, unexpected results were obtained and it was found necessary to carry out a detailed study, the results of which are described in the present paper.

Ladenburg[3] reports the preparation of triphenylsilicane, melting at 200–203°, by the action of sodium and a little benzene upon triphenyl silicon bromide. On the face of it, this reaction seems a little improbable, especially in view of the fact that the corresponding triphenylstannane, and triphenylgermane, recently prepared, have been found to melt at

---

[1] This paper is constructed from a portion of the Dissertation presented by Harry H. Reynolds to the Faculty of the Graduate School of Brown University, in June, 1928, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Rice Fellow, 1925–1926; Metcalf Fellow, 1926–1927.

[3] Ladenburg *Ber.*, **40**, 2278 (1907).