

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOBART COLLEGE]

ACTION OF HYDROGEN CHLORIDE ON STANNANES OF THE TYPE $R_2SnR'_2$

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RECEIVED JUNE 10, 1931

PUBLISHED AUGUST 5, 1931

In a previous paper¹ the action of halogens on some mixed stannanes was discussed. It was shown that the replacement series of some organic groups in decreasing order of ease of removal from tin by halogen is phenyl, benzyl, methyl, ethyl and *n*-propyl. F. B. Kipping,² on halogenating certain mixed stannanes, found that the ease with which various radicals are removed by iodine from a molecule containing two or three different groups decreases in the order: *o*-tolyl, *p*-tolyl, phenyl and benzyl. Hence the replacement series based on the halogenation reaction becomes: *o*-tolyl, *p*-tolyl, phenyl, benzyl, methyl, ethyl and *n*-propyl.

It was considered of interest to ascertain whether or not this order is observed when mixed stannanes are treated with dry hydrogen chloride. Kipping states that the order in which the groups are removed from his unsymmetrical stannanes by warm or hot concentrated hydrochloric acid solutions is in general the same as that with iodine. He notes one exception: tribenzylethylstannane when refluxed with hydrochloric acid yields tribenzylstannyl chloride.

To simplify the problem it was decided in this investigation to prepare symmetrical stannanes of the type $R_2SnR'_2$ and to treat these with dry hydrogen chloride under conditions such that two groups, and only two groups, would be removed. Examination of the resulting dichloride would then show which groups had been removed. For this purpose dimethyldiethylstannane, diethyldi-*n*-propylstannane, and diphenyldiethylstannane were prepared and treated with dry hydrogen chloride at temperatures such that two groups were removed. If the above replacement series of groups is valid in connection with this reaction, one would predict (1) that both methyl groups would be removed from dimethyldiethylstannane, (2) that both ethyl groups would be removed from diethyldi-*n*-propylstannane, and (3) that both phenyl groups would be removed from diphenyldiethylstannane. A study of the reaction products showed them to be (1) methylethylstannyl dichloride, (2) ethyl-*n*-propylstannyl dichloride and (3) diethylstannyl dichloride. In the first two instances the two groups substituted by the chlorine of the hydrogen chloride were one of each kind.

Experimental Part

Preparation of the Stannanes.—Dimethyldiethylstannane, $(CH_3)_2(C_2H_5)_2Sn$, was prepared by the Grignard reaction from methylmagnesium iodide and diethylstannyl

¹ Bullard, THIS JOURNAL, 51, 3065 (1929).

² F. B. Kipping, J. Chem. Soc., 131, 2365 (1928).

dichloride. It was purified by distilling under reduced pressure. It distilled at 32° under 14 mm. pressure and at 132° under atmospheric pressure; yield of the pure stannane, 75% of the theoretical.

Anal. Subs., 0.1351: SnO₂, 0.0986. Calcd. for (CH₃)₂(C₂H₅)₂Sn: Sn, 57.40. Found: Sn, 57.48. *Mol. wt.* Subs., 0.2248, 0.1334, 0.2418: C₆H₆, 21.42, 19.78, 21.47: Δ*t.*, 0.261, 0.167, 0.279. Calcd. for (CH₃)₂(C₂H₅)₂Sn: mol. wt., 206.8. Found: mol. wt., 205.9, 206.6, 206.6.

Diethyldi-*n*-propylstannane, (C₂H₅)₂(*n*-C₃H₇)₂Sn, was similarly prepared by the Grignard reaction using *n*-propyl bromide and diethylstannyl dichloride. It was purified by distilling under reduced pressure. It boiled at 84.5° under 10 to 11 mm. pressure. Under atmospheric pressure it distilled at 205 to 207° with slight decomposition; yield of the pure stannane, 88% of the theoretical.

Anal. Subs., 0.2282, 0.2534: SnO₂, 0.1307, 0.1448. Calcd. for (C₂H₅)₂(*n*-C₃H₇)₂, Sn: Sn, 45.15. Found: Sn, 45.11, 45.01. *Mol. wt.* Subs., 0.1570, 0.3976: C₆H₆, 20.15, 19.82: Δ*t.*, 0.155, 0.406. Calcd. for (C₂H₅)₂(*n*-C₃H₇)₂Sn: mol. wt., 262.9. Found: mol. wt., 257.4, 253.0.

Diphenyldiethylstannane, (C₆H₅)₂(C₂H₅)₂Sn, was likewise prepared by the Grignard reaction from ethylmagnesium bromide and diphenylstannyl dichloride. It was purified by distilling under reduced pressure. It boiled at 155–157° at 4 mm. pressure; yield of the pure stannane, 78.5% of the theoretical.

Anal. Subs., 0.3513, 0.3457: SnO₂, 0.1601, 0.1575. Calcd. for (C₆H₅)₂(C₂H₅)₂Sn: Sn, 35.88. Found: Sn, 35.90, 35.89.

Treatment of Dimethyldiethylstannane with Dry Hydrogen Chloride.—Dry hydrogen chloride was bubbled through 10.89 g. of the stannane contained in a round-bottomed flask. An oil-bath was placed around the flask and the temperature was gradually raised to 140–145° over a period of two hours. The temperature was then maintained at this point for two hours more. On cooling, the contents of the flask solidified. The product was recrystallized from hot petroleum ether; 10.67 g. was obtained. The crystals melted at 52°; yield, calculated as methylethylstannyl dichloride, (CH₃)(C₂H₅)SnCl₂, 86.7% of the theoretical.

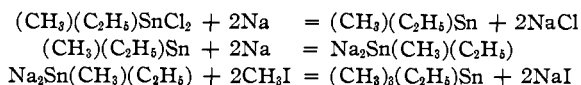
Anal. Subs., 0.1812, 0.2100: SnO₂, 0.1167, 0.1356. Subs., 0.2015, 0.2724: AgCl, 0.2438, 0.3319. Calcd. for (CH₃)(C₂H₅)SnCl₂: Sn, 50.80; Cl, 30.35. Found: Sn, 50.73, 50.86; Cl, 29.93, 30.14. *Mol. wt.* Subs., 0.2323, 0.3860: C₆H₆, 20.44, 20.44: Δ*t.*, 0.248, 0.405. Calcd. for (CH₃)(C₂H₅)SnCl₂: mol. wt., 233.7. Found: mol. wt., 234.6, 238.7.

Some of the methylethylstannyl dichloride was converted into the oxide by dissolving it in water and treating this solution with sodium hydroxide solution. The resulting precipitate was filtered, washed with water, alcohol, ether, and then dried.

Anal. Subs., 0.3652, 0.2618: SnO₂, 0.3065, 0.2202. Calcd. for (CH₃)(C₂H₅)SnO: Sn, 66.40. Found: Sn, 66.10, 66.25.

Methylethylstannyl dichloride was converted into trimethylethylstannane by treatment with sodium and methyl iodide in liquid ammonia. On dissolving 0.5049 g. of the dichloride in liquid ammonia, a clear solution was obtained. Sodium, in weighed amounts, was added to this solution. When 0.0913 g., approximately two atoms of sodium per molecule of dichloride, had been added a yellow gummy precipitate had formed. This was presumably the methylethyltin free group. The further addition of 0.0454 g. of sodium, approximately one more atom of sodium per molecule of dichloride, caused the free group to dissolve and gave a yellow solution. The addition of a further 0.0449 g. of sodium resulted in the formation of a deep red solution of the diso-

dium methylethylstannide, $\text{Na}_2\text{Sn}(\text{CH}_3)(\text{C}_2\text{H}_5)$. A very small amount of sodium in addition gave a deep blue solution, showing that the end-point of the reaction had been passed with this last addition. Methyl iodide was then added until a clear colorless solution was obtained. This produced a white precipitate. On evaporating the ammonia and vapor distilling with ammonia gas through a condenser cooled with liquid ammonia, a few drops of a liquid boiling at 109° (uncorr.) was obtained. Trimethylethylstannane, $(\text{CH}_3)_3(\text{C}_2\text{H}_5)\text{Sn}$, boils at 108.2° corr.³ The reactions involved in the above transformations are therefore



The identification of the trimethylethylstannane formed by these reactions gives rather conclusive proof that the product of the action of hydrogen chloride on dimethyldiethylstannane is methylethylstannyl dichloride.

Treatment of Diethyldi-*n*-propylstannane with Dry Hydrogen Chloride.—Dry hydrogen chloride was bubbled through 4.778 g. of the stannane for four hours at 100° . The solid product was recrystallized from hot petroleum ether; 3.25 g. was obtained; yield, calculated as ethyl-*n*-propylstannyl dichloride, 68.9% of the theoretical. The reaction had not been run quite to completion because the piercing odor of a monoalide was present. The purified substance melted at 53° .

Anal. Subs., 0.1653, 0.1761: SnO_2 , 0.0961, 0.1021. Subs., 0.2045, 0.2465: AgCl , 0.2247, 0.2691. Calcd. for $(\text{C}_2\text{H}_5)(n\text{-C}_3\text{H}_7)\text{SnCl}_2$: Sn, 45.35; Cl, 27.10. Found: Sn, 45.79, 45.67; Cl, 27.18, 27.01.

Treatment of Diphenyldiethylstannane with Dry Hydrogen Chloride.—Dry hydrogen chloride was bubbled for forty minutes through 15.6 g. of the stannane heated at $150\text{--}160^\circ$. The escaping vapors were passed through a small water condenser. A liquid was obtained which was identified as benzene. The solid residue in the reaction flask was crystallized from petroleum ether; 10.46 g. was obtained; yield, calculated as diethylstannyl dichloride, 89.6% of the theoretical. The purified crystals melted at 84° . Diethylstannyl dichloride melts at $84\text{--}85^\circ$.⁴

The authors wish to acknowledge their indebtedness to the Warren Fund of the American Academy of Arts and Sciences for a grant which assisted in defraying the expenses of this investigation.

Summary

The preparation of dimethyldiethylstannane, diethyldi-*n*-propylstannane and diphenyldiethylstannane has been described.

On treating dimethyldiethylstannane with dry hydrogen chloride under conditions such that two groups are substituted by chlorine, one methyl group and one ethyl group are removed with the resulting formation of methylethylstannyl dichloride.

Diethyldi-*n*-propylstannane on similar treatment yields ethyl-*n*-propylstannyl dichloride.

Diphenyldiethylstannane, however, on similar treatment yields diethylstannyl dichloride.

³ Bullard and Haussmann, *J. Phys. Chem.*, **34**, 746 (1930).

⁴ Pfeiffer, *Z. anorg. Chem.*, **68**, 102 (1910).

The replacement series of organic groups as derived from the halogenation of mixed stannanes is not generally applicable and must be restricted in use to the reaction from which it was derived.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BARNARD COLLEGE]

THE FRIEDEL AND CRAFTS REACTION WITH MALEIC ANHYDRIDE AND RESORCINOL DIMETHYL ETHER. THE ADDITION OF AROMATIC ETHERS TO UNSATURATED SUBSTANCES

BY GRACE POTTER RICE

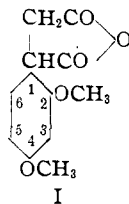
RECEIVED JUNE 11, 1931

PUBLISHED AUGUST 5, 1931

Several examples of the reactivity of maleic anhydride in addition reactions have been recorded in the literature in recent years. Diels and Alder¹ have studied the reactions which this anhydride and other substances, having extremely reactive double linkages, undergo when treated with a large and varied list of unsaturated substances. So specific is this type of reaction that it has been used by Windaus² to prove that a conjugated system of double linkages in an ergosterol derivative is destroyed by irradiation, since the irradiated product failed to react with maleic anhydride.

Kuhn and Wagner-Jauregg³ have studied the addition of maleic anhydride to polyenes and very recently Conant and Scherp⁴ have obtained evidence that a reaction takes place between maleic anhydride and free radicals.

In this Laboratory it has now been found that maleic anhydride combines with resorcinol dimethyl ether in the presence of aluminum chloride to give a saturated anhydride, dimethoxyphenylsuccinic anhydride (I). This reaction can be explained by a mechanism involving a 1,4-addition to maleic anhydride. The anhydride I was unexpectedly obtained, along with other substances, when the Friedel and Crafts reaction with maleic anhydride and resorcinol dimethyl ether was carried out for the purpose of preparing dimethoxybenzoylacrylic acid, II. The fact that this unsaturated acid has been shown to form an addition product with resorcinol dimethyl ether in the presence of aluminum chloride may account in part for the low yield.



¹ Diels and Alder, *Ann.*, **460**, 98 (1928); *Ber.*, **62**, 554, 2081, 2087 (1929); *Ann.*, **486**, 191, 202, 211 (1931).

² Windaus, Gaede, Köser and Stein, *ibid.*, **483**, 27 (1930).

³ Kuhn and Wagner-Jauregg, *Ber.*, **63**, 2662 (1930).

⁴ Conant and Scherp, *THIS JOURNAL*, **53**, 1941 (1931).