this change in structure causes a very great lowering in the physiological activity of the compound.

Summary

1. It has been found that while pyrrole can be reduced catalytically to the tetrahydro derivative, the methyl and carbethoxy substituted pyrroles could not be similarly reduced.

2. γ-Pyrrolidinopropyl benzoate and γ-pyrrolinopropyl benzoate have been prepared and tested pharmacologically as local anesthetics. It was found that the presence of the double bond in the latter greatly reduces its anesthetic activity. The pyrrolidino derivative was shown to have greater anesthetic action than the corresponding piperidino derivative. It is pointed out that this was an unexpected relationship, since data on other series of anesthetics indicated that the reverse should be true.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOBART COLLEGE]

SOME DERIVATIVES OF TRIMETHYLETHYLSTANNANE

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The study of the organic compounds of tin has been continued by investigating certain derivatives of trimethylethylstannane, $(CH_3)_3C_2H_5Sn$. The hydride, dimethylethylstannane, $(CH_3)_2C_2H_5SnH$, derived from trimethylethylstannane by the substitution of a hydrogen atom for a methyl group, is of particular interest. It is oxidized by the air, being converted into the corresponding hydroxide. The reaction is represented by the equation $2(CH_3)_2C_2H_5SnH + O_2 = 2(CH_3)_2C_2H_5SnOH$. This oxidation is interesting in view of the fact that trimethylstannane, $(CH_3)_3SnH$, prepared by Kraus and Greer[1] is stable in the air, whereas triphenylstannane, $(C_6H_5)_3SnH$, prepared by Chambers and Scherer[2] oxidizes in the air to hexaphenylstanno-ethane, $(C_6H_5)_3SnSn(C_6H_5)_3$, with the formation of water.

Trimethylethylstannane, $(CH_3)_3C_2H_5Sn$.—This compound has been prepared by Cahours[3] from trimethylstannyl iodide and zinc diethyl, and also by Pope and Peachey[4] by the use of the Grignard reaction. The following method may also be used to advantage.

Trimethylstannyl bromide, $(CH_3)_3SnBr$, was dissolved in liquid ammonia and converted into the sodium salt by adding two atoms of sodium per mole of bromide. On adding ethyl bromide slowly the yellow color of the

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[1] Kraus and Greer, THIS JOURNAL, **44,** 2629 (1922).

[2] Chambers and Scherer, *ibid.*, **48,** 1054 (1926).

[3] Cahours, *Ann.*, **122,** 48 (1862).

[4] Pope and Peachey, *Proc. Chem. Soc.*, **19,** 290 (1903).

sodium salt was discharged and trimethylethylstannane was precipitated. The reaction took place as follows: $(CH_3)_3SnNa + C_2H_5Br = (CH_3)_3C_2H_5Sn + NaBr$. The ammonia was allowed to evaporate and water was added. The lower layer of colorless oil was separated, dried over anhydrous calcium chloride and distilled. That portion boiling at 107–108° was collected as the pure stannane; yield, 80%.

Mol. wt. Subs., 0.4158, 0.6448: C_6H_6, 21.30, 21.30; Δt, 0.515, 0.784. Calcd. for $(CH_3)_3C_2H_5Sn$: mol. wt., 192.7. Found: 189.5, 193.1; av. 191.3.

Anal. Subs., 0.3830, 0.5569: SnO_2, 0.2996, 0.4374. Calcd. for $(CH_3)_3C_2H_5Sn$: Sn, 61.60. Found: 61.61, 61.86.

Bromination of Trimethylethylstannane.—The stannane was cooled in running water and the calculated amount of a carbon tetrachloride solution of bromine was slowly added. Bromination took place readily. The reaction mixture was fractionally distilled and the portion coming over at 175–180° was collected.

Anal. Subs., 0.4890, 0.2321, 0.1091: AgBr, 0.3621, 0.1682, 0.0792. Calcd. for $(CH_3)_2C_2H_5SnBr$: Br, 31.02. Found: 31.51, 30.84, 30.85.

Ammonia gas was passed into a carbon tetrachloride solution of dimethylethylstannyl bromide. A white precipitate of the ammonia complex was obtained. This complex salt was not stable, for on standing it softened and the odor of the bromide became evident.

Dimethylethylstannane, $(CH_3)_2C_2H_5SnH$.—Dimethylethylstannyl bromide was dissolved in liquid ammonia and converted into the sodium salt by adding two atoms of sodium per mole of bromide. Excess ammonium bromide was then slowly added. The reaction proceeded as follows: $NaSnC_2H_5(CH_3)_2 + NH_4Br = (CH_3)_2C_2H_5SnH + NaBr + NH_3$. When the reaction was completed, the reaction tube was connected to a receiver immersed in liquid ammonia and the ammonia in the reaction tube was allowed to evaporate. The reaction tube was then warmed in a water-bath at 100° while a slow stream of ammonia gas was passed through the tube. The stannane was thus vapor-distilled from the reaction tube into the cooled receiver. The stannane boils at 90° under atmospheric pressure.

Anal. Subs., 0.4930: SnO_2, 0.4135. Calcd. for $(CH_3)_2C_2H_5SnH$: Sn, 66.42. Found: Sn, 66.07.

Mol. wt. Subs., 0.1290, 0.0843: 387 cc. (33.5 and 24.5 mm. at 22°). Calcd. for $(CH_3)_2C_2H_5SnH$: mol. wt., 178.7. Found: 182.9, 177.3; av., 180.1.

Oxidation of Dimethylethylstannane.—In order to preserve the stannane in the pure state it was found necessary to keep it sealed in tubes under nitrogen. The capillary at the end of the tube containing some dimethylethylstannane was broken, thus allowing the air to enter. After a few days the tube contained a mass of white, needle-like crystals which were found to be very hygroscopic.

Anal. Subs., 0.0883, 0.1382: SnO_2, 0.0681, 0.1072. Calcd. for $(CH_3)_2C_2H_5SnOH$: Sn, 60.96. Found; Sn, 60.75, 61.10.

Dimethylethylstannyl hydroxide was also prepared from dimethylethylstannyl bromide by treating the bromide with 30% sodium hydroxide solution. The reaction mass was extracted with ether, the ether solution dried over anhydrous calcium chloride and the ether removed by boiling under reduced pressure at room temperature. There remained a mass of white crystals which, too, were hygroscopic.

Anal. Subs., 0.2492: SnO_2, 0.1926. Calcd. for $(CH_3)_2C_2H_5SnOH$: Sn, 60.96. Found: Sn, 60.88.

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Summary

1. Trimethylethylstannane has been prepared in yields of 80% by treating sodium trimethyl stannide with ethyl bromide.

2. On brominating trimethylethylstannane a methyl group is removed and dimethylethylstannyl bromide is formed.

3. Dimethylethylstannane has been prepared by treating sodium dimethyl ethyl stannide in liquid ammonia with ammonium bromide.

4. On slow atmospheric oxidation of dimethylethylstannane there is formed dimethylethylstannyl hydroxide.

GENEVA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS OF NORTHWESTERN UNIVERSITY]

THE ACTION OF BASES ON CERTAIN MERCURATED ANILINES

BY FRANK C. WHITMORE, E. R. HANSON AND F. L. CARNAHAN[1]

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A reaction which has received considerable study in this Laboratory is the conversion of mercury compounds of the type RHgX into the so-called "mercuri-*bis*" compounds of the type R_2Hg, in which both valences of the mercury are attached to carbon.

$$2\ RHgX \rightleftharpoons R_2Hg + HgX_2$$

This reaction readily goes to the left without any special precautions. It can be made to go to the right by a great variety of reagents, such as iodides, sulfides, thiosulfates, cyanides, sodium stannite and metals such as copper and sodium. For some time the working hypothesis in this Laboratory was that the formation of the mercuri-*bis* compounds could be brought about by "any reagent which removes mercuric ions more completely than does sodium hydroxide." This hypothesis proved useful but

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[1] This work was carried on during the years 1923–1927 under grants from the Public Health Institute of Chicago.