

Pauly's reagent) the crude hydrochloride gave three red spots with  $R_f$  0.74 (strong),  $R_f$  0.83 (strong) and  $R_f$  0.95 (weak). By comparison, histamine under the same conditions gave a spot at  $R_f$  0.65, as reported by Ames and Mitchell.<sup>7</sup>

The crude hydrochloride described above was dissolved in 300 cc. of water. To this solution was added a hot solution of 20 g. of picric acid in 250 cc. of water. A black oil separated immediately. The mixture was refluxed for a short time, decanted from an insoluble precipitate which was again extracted with 250 cc. of boiling water. Upon conversion to the hydrochloride the residue gave only a slight pink color with Pauly's reagent and was discarded. Upon cooling the combined aqueous layers, yellow crystals separated, which were filtered and washed with water and ether in order to remove picric acid; yield nearly pure picrate, 1.7 g., m.p. 223–226° (dec.); this corresponds to 0.4 g. of dimethylhistamine or about 0.06% of the original weight of the seeds used. Four recrystallizations from water with very little loss of material raised the m.p. to 229–230°, either alone or in mixture with an authentic sample of synthetic  $N\alpha, N\alpha$ -dimethylhistamine dipicrate.<sup>9</sup>

*Anal.* Calcd. for  $C_7H_{13}N_3 \cdot 2C_6H_2N_2O_7$ : C, 38.20; H, 3.21; N, 21.10. Found: C, 38.12; H, 3.03; N, 20.86.

A sample of the picrate was dissolved in a small amount of 50% ethanol and shaken with sufficient anion exchange resin Dowex 1-X4 in the chloride form to decolorize the solution. Upon evaporation the dihydrochloride was obtained, m.p. 182–184°, either alone or in mixture with an authentic sample of synthetic  $N\alpha, N\alpha$ -dimethylhistamine dihydrochloride.<sup>9</sup>

*Anal.* Calcd. for  $C_7H_{13}N_3 + 2HCl$ : C, 39.63; H, 7.13; N, 19.81; Cl, 33.43. Found: C, 39.50; H, 7.14; N, 19.40; Cl, 33.31.

The infrared spectra of both salts and of the corresponding authentic synthetic salts were superimposable. With paper chromatography both the isolated material and the synthetic sample gave a single spot at  $R_f$  0.81 under the conditions described above.

The mother liquor from the crude picrate, above, was evaporated to dryness, washed with ether to remove excess picric acid and the amorphous picrate which remained was converted into the hydrochloride, yield 5.0 g. of black resin. On paper chromatography a sample showed a single spot at  $R_f$  0.73. This product is now being investigated.

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### Addition of Dibutyltin Hydride to Tetrafluoroethylene

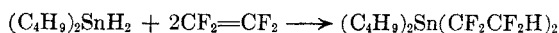
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Silanes have been reported to add to fluoroolefins *via* the inorganic free radicals, and the pos-

sibility of extending this type of reaction to various metal hydrides has been considered.<sup>1</sup> However, no such addition of a metal hydride to a fluoro-olefin to form a fluoro-organometallic compound has been reported up to this time.

Tin hydrides have previously been added to a number of olefins such as styrene and acrylonitrile to form new organotin compounds.<sup>2</sup> This reaction evidently does not involve free radicals since it occurs in the presence of radical inhibitors. Extension of the reaction to include tetrafluoroethylene as the olefin has now been accomplished with di-*n*-butyltin hydride at 90°. Like the other adducts from tin hydrides, this fluoroalkyltin compound is readily formed without the aid of a free radical initiator.



### EXPERIMENTAL

Di-*n*-butyltin hydride, b.p. 56–59° (5 mm.), was prepared by reduction of di-*n*-butyltin dichloride with lithium aluminum hydride.<sup>3</sup> A mixture of 4.0 g. (0.017 mole) of di-*n*-butyltin hydride and 10 g. (0.10 mole) of tetrafluoroethylene was heated in an 80-ml. shaker tube at 90° under autogenous pressure for 4 hr. Distillation of the liquid product gave 2.1 g. (28% conversion based on the hydride) of di-*n*-butylbis(1,1,2,2-tetrafluoroethyl)tin, b.p. 46–47° (0.2 mm.).

*Anal.* Calcd. for  $C_{12}H_{20}F_8Sn$ : C, 33.13; H, 4.64; F, 34.94; Sn, 27.29. Found: C, 33.14; H, 4.39; F, 34.52; Sn, 27.88. The structure was confirmed by determination of the  $F^{19}$  and  $H^1$  spectra by nuclear magnetic resonance. The expected doublet for fluorine and triplet for hydrogen, characteristic of the  $CF_2H$  group, were found. The presence of the Sn— $CF_2$  group was established by the observation that this fluorine peak had satellites attributable to splitting by tin isotopes.

There was no evidence that the product, a clear colorless oil, decomposed to tin fluorides and trifluoroethylene under the conditions of the reaction.

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### Formation of an *N*-Acylamide in Peptide Synthesis

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The reaction between mixed carbonic-carboxylic anhydrides and amines has by now been successfully applied to the synthesis of a large number of

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