

From these experimental results, it is conceivable that the activation of papain by rongalite relates to the appearance of aldehyde group. The further work is being continued.

21. Preparation of Tertiary Aryl Stibine

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Tertiary stibines are prepared ordinarily by the Grignard's method. In the course of the study of stibonic acids, it has been found that the antimony trichloride can be converted to the tertiary aromatic stibines by the aryldiazonium fluoborate and zinc dust.

Benzenediazonium fluoborate (1 mol.) was added to the acetic anhydride (600 cc.) solution of antimony trichloride (1/3 mol.) under cooling and then zinc dust (1 mol.) was added during two hours, (temp. below 20°). In each addition of a small portion of zinc, diazonium salt decomposed with the liberation of nitrogen gas. After overnight, the filtered reaction product was poured into the water. The resulted oily fraction was digested with sodium carbonate and extracted with ether. Ether insoluble part was recrystallized from alcohol and phenylstibinous oxide was isolated in the yield of 8% (M. P. 150°). When ether soluble part was shaken with dilute sulphuric acid, diphenylstibinous oxide was precipitated as the sulphate. After neutralization of the sulfate with sodium carbonate diphenylstibinous oxide was separated as a fine colourless crystal (yield 30%, M. P. 77°). Evaporating the ether solution of neutral part, triphenylstibine was obtained as a viscous oil (yield 12%).

Varying the ratio of antimony trichloride (1 mol. and 1/6 mol.) or using the Guttermann's copper powder, the reaction took place with a lower yield of stibine derivatives.

p-Tolyldiazonium fluoborate and antimony trichloride in the same condition with zinc, were converted to p-tolylstibine derivatives which composed of mainly tri-p-tolylstibine (42%), and a small quantity of the corresponding diaryl and monoaryl stibine chloride. (4% and 8%).

p-Nitrophenylstibine derivatives were resulted in the yield of 24% (mixture), when the corresponding diazonium fluoborate is decomposed as the same manner, but the separation of the three classes of stibine derivatives could not be attained.