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30 Charles River Road, Cambridge, Massachusetts

IRVIN STEWART, Executive Secretary

FSB-HBS--

February 18, 1943

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Dr. Melvin Calvin
Department of Chemistry
University of California
Berkeley, California

Dear Dr. Calvin:

As a result of my visit with Mr. W. J. Harshaw, President of Harshaw Chemical Co., Cleveland, Ohio, during my recent trip to Ames, it appears that little is known about direction fluorination of aromatic compounds. Before asking Harshaw to become involved in a research program, Mr. Stevenson believes that you should have Dr. Geissman make up sufficient 3-fluorosalicylaldehyde to permit you to make tests on the chelate and to forward a quantity to Catteral at MIT for engineering data.

From talking with Mr. Harshaw and his associates it appears that Harshaw Chemical's principal interest in fluorine is in the manufacture of anhydrous HF, BF_3 , HBF_4 , and SbCl_2F_4 for use with aliphatic hydrocarbons. The SbCl_2F_4 is used principally for making the Freons from $\text{CCl}_4 + \text{C}_2\text{Cl}_6$ and does not react even reasonably well with halogenated aromatics.

The best method is to get F into the benzene nucleus is by diazotization of the amine, treating with HBF_4 , and thermally decomposing the precipitated resulting diazonium compound, as you have done. The decomposition is difficult to control, as you may know, and the Harshaw group were skeptical about handling commercial quantities of it. Large volumes of wet BF_3 would have to be handled. This is a hazardous operation requiring very special handling. It would only be feasible for commercial application if this gas were recovered, concentrated, and used again.

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Inquiry relative to possible yields of fluoro derivatives brought forth a number of guesses ranging from 1% for replacement of chlorine in aromatic nuclei to 25-30% by diazotization of the amine. It is possible that with a substitute F acting much like hydrogen on the ring, the Reimer Tieman or allyl ether method should work better with a fluorphenol than with o-chlorphenol to form aldehydes.

Any information or improvements in yield that you or Dr. Geissman can get should be helpful in the overall problem.

With kind regards,

Sincerely yours



F. S. Bacon
Assistant to the Chief
E. P. Stevenson
Section 11.1
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CC - Dr. T. A. Geissman
- Drs. J. H. Rushton
and S. S. Prentiss