



OFFICE FOR EMERGENCY MANAGEMENT

NATIONAL DEFENSE RESEARCH COMMITTEE

OF THE

OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

729790

JAMES B. CONANT, Chairman
RICHARD C. TOLMAN, Vice Chairman
ROGER ADAMS
CONWAY P. COE
KARL T. COMPTON
FRANK B. JEWETT
MAJ. GEN. R. C. MOORE
CAPT. LYBRAND P. SMITH

1530 P STREET NW.
WASHINGTON, D. C.

30 Memorial Drive, Cambridge, Massachusetts

IRVIN STEWART, Executive Secretary FSB-HBS

May 19, 1943

R

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

BEST COPY AVAILABLE

Dear Dr. Calvin:

Your report covering the period April 1-May 1, 1943, has been read by Mr. Stevenson and myself with much interest and the program discussed at some length.

The fluoro compound still looks promising. Could you send a pound of the fluoro chelate to Dr. Catterall at MIT on receipt of this letter. We are all anxious to get it on the MIT test setup. As soon as you have 35 lbs. of the fluoro chelate available it should be tried out by the ADL group in the flat bed reactor.

A few questions were raised relative to the data submitted on your cycling tests. 1) What temperature cooling water was used during the absorption? 2) Did you get complete absorption in 3-1/2 min. @ 20 psi? 3) Was the 6 minute desorption @ 100° C. and 1/3 atm. pressure used to obtain complete desorption?

In discussing the synthesis a somewhat different approach occurred to me. Your synthesis starts with o-anisidine, which I understand is available at a reasonable price in quantity. Ortho anisidine is prepared from o-nitrochlorbenzene by methoxylation followed by reduction, at least I am sure Monsanto still uses this process. I worked it through the pilot plant stage for Monsanto back in 1919. We might, therefore, consider that o-nitrochlorbenzene is the starting intermediate. Fundamentally we must go back to benzene, but for argument let's start with o-nitrochlorbenzene.

Your process consists of the following six steps:
o-nitrochlorbenzene -- o-nitroanisole -- o-anisidine -- o-fluoroanisole -- o-fluorophenol -- 3-fluoro 2-hydroxy-benzaldehyde. Thus far, your

(over)
CLASSIFICATION CANCELLED OR

CHANGED TO Unclassified
BY AUTH. CG DAR-1 43.1

BY Don J. O. FDC DATE 4/3/96
3rd Fl Building 400 3/3/16

1259714

~~CONFIDENTIAL~~
~~CONFIDENTIAL~~

-2-

overall yield is not too hopeful from a commercial point of view.

In thinking about this synthesis, another series of compounds came to mind, consisting of five steps as indicated, about which I will comment below: o-nitrochlorbenzene → sodium o-nitrophenate → o-aminephenol → o-fluorophenol → to fluoroaldehyde.

During World War I o-nitrochlorbenzene was an unwelcome by-product in the plant in which I was working, so considerable research time was spent on its utilization.

By treating with NaOH under pressure at elevated temperature a 95% plus yield of sodium o-nitrophenate was obtained. This compound is a brilliant orange red to red crystal. I do not recall definitely the concentration of the NaOH or temperature, but I think it was 10% and 120-130° C. respectively.

Sodium o-nitrophenate can be quantitatively converted to o-amino phenol by Na₂S₂ in aqueous solution. This step was tricky, requiring stoichiometrical quantities and close control of temperature. It should be around 106-110° C., as I recall, and was obtained by adjusting the water content of the reaction mixture. Good agitation was essential, and when neutralizing with acid, it must not be carried to the acid side. When properly done, the o-amino phenol appears as beautiful white crystals which are stable to light and air for a long period of time. The filtrate should be slightly brownish, but have no yellow tinge. A yellow color indicates an excess of sulphur in the Na₂S₂ and will stain the crystals of o-amino phenol.

Ortho amino phenol under proper conditions can be diazotized readily without danger of coupling with itself, and it should be possible to form the borofluoride from this diazonium compound. I did not do the work on this step and am not familiar with the technique. I may have it in some of my old notes. I do know, however, that a number of dyestuffs were made from o-amino phenol in the laboratory, but none were ever put on the market.

to o-amino phenol

The reduction of sodium o-nitrophenate/was carried out in 100 lb. lots satisfactorily. The production of sodium o-nitrophenate was made in 1000 lb. batches, and the product was ultimately used in some sulphur dyestuffs.

~~CONFIDENTIAL~~

This suggestion is passed on for what it may be worth. I may be able to locate my old data on this work if you are interested.

At any rate, I would be pleased to have your comments.

Sincerely yours

F. S. Bacon

F. S. Bacon
Assistant to E. P. Stevenson
Chief
Division 11

1259716