

Monsanto

FROM W. B. Bennett (4-4803) Research Dept. N-2-B
(NAME-LOCATION-PHONE)

DATE : December 21, 1982
SUBJECT : First Synthesis of TCDD
REFERENCE :
TO : T. M. Bistline - E2ND
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CC:

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In our meeting on December 17, I was requested to retrieve the 1957 article in Journal of the American Chemical Society by Henry Gilman and J. J. Dietrich (Iowa State University) in which the first synthesis of TCDD was reported. I had obtained this reference as the first synthesis of TCDD from the EPA document "Dioxins, Volume III, Assessment of Dioxin-Forming Chemical Processes", June, 1980.

The Gilman article was retrieved only to discover that TCDD was not reported. 2,3,7,8-Tetrabromodibenzo-p-dioxin was made by bromination of dibenzo-p-dioxin until no more bromine was taken up. Structure was theorized from elemental analysis and infrared spectrum. The authors were interested only in showing where bromine or chlorine attached themselves to the dibenzo-p-dioxine molecule. The EPA document was incorrect in assigning TCDD analysis to this paper.

Chemical Abstracts was then searched for TCDD. There were two references in 1957 (and none in prior years). Apparently W. Saundermann, H. Stockmann, and R. Casten reported the first synthesis of TCDD in Chemische Berichte 90, 690-692 (1957). They made it by chlorination of dibenzo-p-dioxin in chloroform. Identification was solely by elemental analysis (C, H, and Cl). They remarked that it caused chloracne in very small quantities. The work was done at the Institute for Wood and Cellulose Chemistry in Hamburg, and was related to work with pentachlorophenol.

Kimmig and Schultz in 1957 reported TCDD was given them among compounds "synthesized by industry". Synthesis and structure proof were not given. Acneogenic activity was shown. It is possible that the Kimmig and Schultz sample was supplied by the Saundermann group.

I have copies of the Gilman and the Saundermann articles (the latter in German) if anyone wishes to review them.

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SUBJECT TO PROTECTIVE ORDER.

W. B. Bennet

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