uct was repeatedly washed with distilled water and dried at 110°. Samples from two different preparations were used in the chlorine determinations. *Anal.* Calcd. for $C_{20}H_{10}O_5I_2$: I, 43.46; Cl, 0.00. Found: I, 35.96, 36.15; Cl, 7.75, 7.80.

It is to be noted that the total determined halogen content indicates the occurrence of some tri- or tetrahalogenation.

Chlorination may have been due to chlorine released by the action of the excess dichloramine-T on chloride ion.[5] Although the presence of some chlorine in the product might be accounted for by adsorption of potassium chloride or dichloramine-T, this is unlikely, as approximately one-sixth of the weight of the product would have to consist of potassium chloride (or an even greater fraction of adsorbed dichloramine-T) to account for all the chlorine present.

It was not possible to prepare pure diiodofluorescein-I_2^{131} using the method[3] for 3,5-diiodo-4-pyridone-I_2^{131}.

Acknowledgment.—This work was supported in part by the Office of Naval Research, Contract No. N8onr 60500.

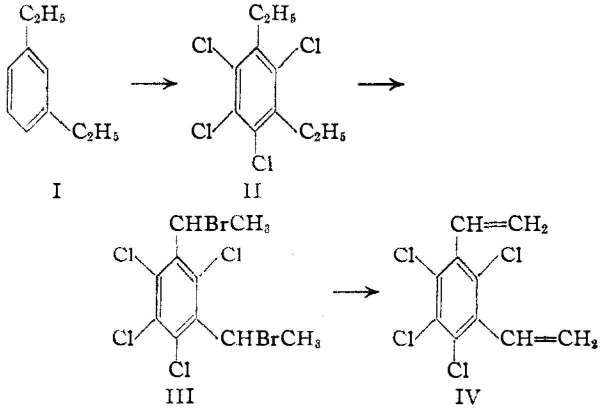
[5] R. A. Bradfield, K. J. P. Orton and I. C. Roberts, *J. Chem. Soc.*, 782 (1928).

RADIOISOTOPE LABORATORY AND
VENABLE CHEMICAL LABORATORY
UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, NORTH CAROLINA RECEIVED MARCH 2, 1951

The Preparation of 1,3-Divinyl-2,4,5,6-tetrachlorobenzene[1]

BY SIDNEY D. ROSS AND MOUSHY MARKARIAN

In a previous report from this Laboratory,[2] we described the preparation of 1,4-divinyl-2,3,5,6-tetrachlorobenzene and its copolymerization with styrene. It is our present purpose to report the preparation of 1,3-divinyl-2,4,5,6-tetrachlorobenzene by the sequence of reactions



Experimental

1,3-Diethyl-2,4,5,6-tetrachlorobenzene (II).—In a 1-liter 3-neck flask equipped with a thermometer, dropping funnel and reflux condenser were placed *m*-diethylbenzene (134 g., 1 mole), obtained from the Dow Chemical Company, and aluminum chloride (5 g.). From the dropping funnel the chlorinating mixture, consisting of sulfuryl chloride (544 g., and sulfur monochloride (5.44 g.), was added slowly, maintaining the temperature at 35–45°. When all of the chlorinating mixture had been added, the cooling bath was removed, and the reaction mixture was allowed to stand at room temperature overnight. Carbon tetrachloride was added, and the solution was decanted from the aluminum chloride complex, washed several times with water and finally dried over magnesium sulfate. The solvent was removed, and the residue was distilled at 11 mm. A mixture of liquid and crystals of b.p. 162–165.5° was obtained. The crystals were filtered and crystallized several times from ethanol to yield 42 g. (15%) of II of m.p. 41–43°.

Anal.[3] Calcd. for $C_{10}H_{10}Cl_4$: C, 43.73; H, 4.00. Found: C, 43.30, 43.44; H, 3.83, 3.76.

II has also been prepared by treating 1,2,3,5-tetrachlorobenzene with ethylene in the presence of aluminum chloride.[4] Most of the 1,3-diethyl-2,4,5,6-tetrachlorobenzene used in this work was obtained by crystallization of the mixed diethyltetrachlorobenzenes obtained from the Dow Chemical Company.

1,3-Bis-(α-bromoethyl)-2,4,5,6-tetrachlorobenzene (III).—Bromine (320 g., 2 moles) was added slowly to II (271.8 g., 1 mole) in carbon tetrachloride (3 liters). The solution was illuminated and maintained at the boiling point by a projection bulb inserted directly into the solution. Removal of the solvent gave 400 g. (92%) of the crude product of m.p. 61–70°. Recrystallization from ligroin (b.p. 90–100°) gave 224 g. (51.5%) of III, m.p. 95–99°. As in the case of the 1,4-isomer this product is undoubtedly a mixture of the *meso* and *dl*-forms.

Anal. Calcd. for $C_{10}H_8Cl_4Br_2$: C, 27.97; H, 1.86. Found: C, 27.70, 27.78; H, 1.70, 1.57.

1,3-Divinyl-2,4,5,6-tetrachlorobenzene (IV).—III (21.4 g., 0.05 mole) was refluxed one hour with sodium hydroxide (6 g., 0.15 mole) in ethanol (200 cc.) and then poured into water. Crystallization of the crude product from ethanol yielded 6.6 g. (47%) of IV, m.p. 53–55°.

Anal. Calcd. for $C_{10}H_6Cl_4$: C, 44.85; H, 2.26. Found: C, 44.90, 44.78; H, 2.53, 2.39.

---

[1] This work was carried out under contract no. W36-039-sc-38110 with the Signal Corps of the United States Army.

[2] S. D. Ross, M. Markarian, H. H. Young, Jr., and M. Nazzewski, THIS JOURNAL, **72**, 1133 (1950).

[3] The microanalyses are by Dr. Carl Tiedcke.

[4] M. Istrati, *Ann. chim. phys.*, [6] **6**, 500 (1885).

RESEARCH LABORATORIES OF
THE SPRAGUE ELECTRIC COMPANY
NORTH ADAMS, MASSACHUSETTS RECEIVED MAY 8, 1951

Spectrophotometric Evidence for the Absence of Free Aldehyde Groups in Periodate-oxidized Cellulose[1]

BY JOHN W. ROWEN,[2] FLORENCE H. FORZIATI[2] AND RICHARD E. REEVES[3]

As a part of an investigation of the application of infrared spectrophotometry to a study of cotton cellulose, it was desired to locate the absorption produced by the C=O stretching vibration of aldehyde groups in oxidized celluloses. Periodate-oxidized cotton cellulose appeared to be a suitable material for the study of free aldehyde groups in cellulose inasmuch as the oxidized anhydroglucose unit is usually assumed to contain two free aldehyde groups as shown in structure I. An alternative structure, II, containing one free aldehyde and one hemiacetal group has also been proposed.[4] However, observations on periodate-oxidized cellulose

---

[1] A report of work done under coöperative agreement with the United States Department of Agriculture and authorized by the Research and Marketing Act. The work is being supervised by the Southern Regional Research Laboratory of the Bureau of Agricultural and Industrial Chemistry.

[2] National Bureau of Standards.

[3] Southern Regional Research Laboratory.

[4] Mitchell and Purves, THIS JOURNAL, **64**, 589 (1942).