tion in rates occurring on the addition of water to the reaction media in these two cases.

Studies of the acidity function in other mixed solvents have been reported by Braude,[4b] and the general similarity of the results is evident. The only point of difference is the disappearance of the maximum in the value of H_0 in dilute acid (0.01 N). Further work is necessary before offering an interpretation of this change.

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Isomerization Accompanying Alkylation. VIII.[1] Reaction of Benzene with 2- and 3-Pentanol

BY HERMAN PINES, WILLIAM D. HUNTSMAN[2] AND V. N. IPATIEFF

It has been found that the alkylation of benzene with ethylcyclopropane in the presence of hydrogen fluoride, aluminum chloride or sulfuric acid gives a mixture of amylbenzenes consisting, in each case, of approximately 63% 2-phenylpentane and 37% 3-phenylpentane.[1] The large amount of isomerization occurring during this reaction suggests that the 2- and 3-pentylcarbonium ions are readily interconvertible in the presence of acidic catalysts. Further evidence for this has been obtained from a study of the alkylation of benzene with 2- and 3-pentanol using aluminum chloride and hydrogen fluoride catalysts.

The monoalkylated product from the reaction of 3-pentanol with benzene in the presence of hydrogen fluoride at 0–5° consisted of 56% 2- and 44% 3-phenylpentane. When aluminum chloride was used as the catalyst at 25–35°, the product consisted of 76% 2- and 24% 3-phenylpentane. In the latter case, the aluminum chloride was added to a solution of the alcohol in benzene to avoid an excess of aluminum chloride in contact with the pentylbenzenes.

Similar results were obtained when 2-pentanol was used as the alkylating agent with aluminum chloride as catalyst. Thus, the monoalkylated product consisted of 60% 2-phenylpentane and 40% 3-phenylpentane. This reaction was previously reported to give 2-phenylpentane.[3]

Similar results were obtained previously[4] when 1-pentanol reacted with benzene in the presence of 80% sulfuric acid at 70°.

Infrared spectral analysis was used in each case to determine the product composition; this was done according to the method described in the preceding publication.[1]

Experimental

1. **3-Pentanol. Hydrogen Fluoride Catalyst.**—The procedure for this type of reaction has been described previously.[5] From 10 g. (0.114 mole) of 3-pentanol, 78 g. (1.0 mole) of benzene and 20 g. (1.0 mole) of hydrogen fluoride, there was obtained 13.8 g. (78% yield) of monoalkylated material, b.p. 190–192°, $n^{20}\text{D}$ 1.4875. The infrared spectrum of the product showed it to consist of 56% 2- and 44% 3-phenylpentane.

Aluminum Chloride Catalyst.—Aluminum chloride, 26.6 g. (0.2 mole) was added in small portions to a well-stirred solution of 17.6 g. (0.2 mole) of 3-pentanol in 78 g. (1.0 mole) of benzene. The temperature was maintained below 35° by occasional cooling in an ice-bath. The mixture was stirred for one hour and then allowed to stand overnight at room temperature. The product was poured into ice-water, washed with 10% hydrochloric acid, 10% sodium hydroxide and water until neutral to litmus. After drying over calcium chloride, distillation gave 23.5 g. (80% yield) of monoalkylated product, b.p. 190–193°, $n^{20}\text{D}$ 1.4877. The infrared spectrum showed that the product consisted of 76% 2- and 24% 3-phenylpentane.

2. **2-Pentanol. Aluminum Chloride Catalyst.**—The procedure of Huston and Hsieh was followed.[3] The monoalkylated product, obtained in 40% yield, had the following constants: b.p. 190–193°, $n^{20}\text{D}$ 1.4878. It consisted, according to infrared spectral analysis, of 60% 2- and 40% 3-phenylpentane.

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[1] For paper VII of this series, see H. Pines, W. D. Huntsman and V. N. Ipatieff, THIS JOURNAL, **73**, 4343 (1951).

[2] Universal Oil Products Predoctoral Fellow, 1947–1950.

[3] R. C. Huston and T. Y. Hsieh, THIS JOURNAL, **58**, 439 (1936).

[4] V. N. Ipatieff, H. Pines and L. Schmerling, *J. Org. Chem.*, **5**, 253 (1940).

[5] H. Pines, A. Edeleanu and V. N. Ipatieff, THIS JOURNAL, **67**, 2193 (1945).

The Purity of Diiodofluorescein-I_2^{131}

BY ARTHUR ROE, RAYMOND L. HAYES[1] AND H. D. BRUNER[1]

Diiodofluorescein containing iodine^{131} is being extensively used as an aid in the location of brain tumors. In a recent paper, Boyack, Moore and Clausen[2] report the preparation of diiodofluorescein-I_2^{131} by iodination of fluorescein with iodine^{131} monochloride. Their method includes a convenient method of preparing iodine^{131} monochloride from dichloramine-T and sodium iodide^{131} with potassium iodide as carrier; they employ a 100% stoichiometric excess of dichloramine-T. When we attempted[3] to adapt this iodinating system to the preparation of 3,5-diiodo-4-pyridone-I_2^{131} the product obtained contained chlorine as well as iodine; it was found necessary to decrease greatly the excess of dichloramine-T in order to obtain the desired chlorine-free diiodopyridone. This observation suggested the possibility that chlorination as well as iodination might also occur in the above-mentioned synthesis of diiodo^{131}-fluorescein. Boyack, Moore and Clausen gave no analysis of their product, stating that a diiodo structure was strongly supported by the fact that all the iodine was consumed in iodination as indicated by the absence of iodine in the filtrate from the reaction product.

We, therefore, prepared samples of diiodofluorescein according to the directions of Moore, *et al.*,[2] (except that no iodine^{131} was used) and analyzed them for chlorine and iodine. The fluorescein used was purified as the diacetate,[4] and the reaction prod-

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[1] Medical Division, Oak Ridge Institute of Nuclear Studies, Oak Ridge, Tennessee.

[2] G. Boyack, G. E. Moore and D. F. Clausen, *Nucleonics*, **3**, No. 4, 62 (1948).

[3] Roe, Hayes and Bruner, *J. Elisha Mitchell Soc.*, **66**, 163 (1950).

[4] W. R. Orndorff and A. J. Hemmers, THIS JOURNAL, **49**, 1272 (1927).

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
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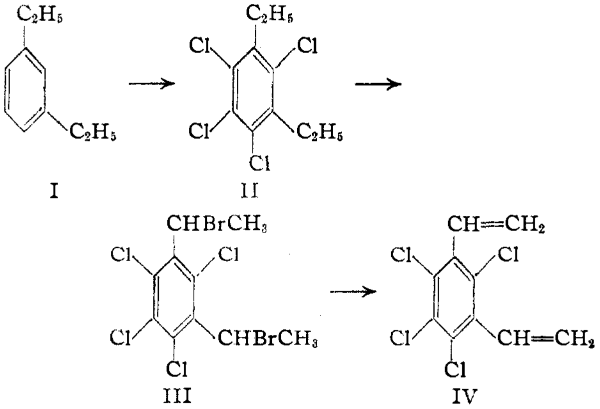
CHAPEL HILL, NORTH CAROLINA RECEIVED MARCH 2, 1951

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.

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[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
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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

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[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).