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.

Acknowledgment.—The authors wish to thank Professor Richard E. Powell for many helpful discussions.

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
UNIVERSITY OF CALIFORNIA
BERKELEY 4, CALIFORNIA RECEIVED JANUARY 20, 1951

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°, $n^{20}D$ 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°, $n^{20}D$ 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°, $n^{20}D$ 1.4878. It consisted, according to infrared spectral analysis, of 60% 2- and 40% 3-phenylpentane.

---

[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 IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY
DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS RECEIVED FEBRUARY 5, 1951

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-

---

[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).