

The quite fair agreement of the correlation in the case of solutions of sulfuric acid in glacial acetic acid with that in the aqueous solutions is impressive. The  $H_0$  values for these superacid solutions are taken from work of Paul and Hammett, which is in agreement with the more extensive work of Hall and Spengeman.<sup>4</sup> One should note that both  $H_0$  and the rate constant for the reaction are about the same in 1 *M* sulfuric acid solution in glacial acetic acid as in 6.5 *M* aqueous solution. This appears to be the first correlation found between a reaction rate and  $H_0$  in glacial acetic acid.<sup>5</sup> The apparent simplicity of the reaction from the experimental point of view and its conveniently measurable rate in quite strongly acid solutions suggest further applications to the study of acid catalysis mechanisms, some of which are being explored at this Laboratory.

(4) M. A. Paul and L. P. Hammett, *THIS JOURNAL*, **58**, 2182 (1936); N. F. Hall and W. F. Spengeman, *ibid.*, **62**, 2487 (1940).

(5) For the correlation of a reaction rate with the essentially different potentiometric  $pH_{HA_0}$  scale of N. F. Hall and J. B. Conant, *ibid.*, **49**, 3047 (1927), see J. B. Conant and G. M. Bramann, *ibid.*, **50**, 2305 (1928).

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### Side-Chain Bromination. III. Fluorobenzyl Bromides

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The photobromination of the fluorotoluenes has not been studied. We found one bromine may be introduced readily into the side-chain under the influence of a strong mercury arc.

**Experimental.**—The ease of side-chain bromination of the fluorotoluenes was determined by the time required to decolorize the bromine solution. The brominations were carried out on 10-g. samples dissolved in 50 ml. of carbon tetrachloride in a round-bottom Pyrex flask fitted with a reflux condenser and calcium chloride outlet tube. A 6-inch mercury arc was placed 0.75 inch from the flask on a hot water-bath. A molar solution of bromine in carbon tetrachloride was added through a dropping funnel as rapidly as the bromine color faded. At the end of the time indicated the solvent was removed under a vacuum and the residue dried and analyzed for side-chain bromine.<sup>1</sup> *o*-Fluorotoluene gave 69.6% active bromine in four minutes; *m*-F 70.9% in 6 min.; *p*-F 76.5% in 16 min.; several other substituted toluenes were included to correlate the results with a previous study.<sup>2</sup> *o*-Bromotoluene decolorized in twenty minutes to give 69.8% side-chain bromine; *m*-Br 70.8% in six minutes; *p*-Br 87.3% in six minutes; *o*-I 14.4% in ten minutes; *m*-I 44.4% in 120 minutes. (The color of the solution made it difficult to determine how rapidly the bromine reacted); 3,5-dimethyl 89.5% in six minutes.

Samples of the three fluorobenzyl bromides were purified by vacuum distillation and found to correspond with those made from fluorobenzyl alcohols; ortho isomer b. p. 84–86° (15 mm.); meta isomer 73–75° (15 mm.); para isomer 85–87° (15 mm.).<sup>3</sup>

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- (1) Sampey, Blitch and King, *THIS JOURNAL*, **70**, 2606 (1948).
- (2) Sampey, Fawcett and Morehead, *ibid.*, **62**, 1839 (1940).
- (3) Shoosmith and Slater, *J. Chem. Soc.*, 214–223 (1926).

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### Limitations of the Anthrone Test for Carbohydrates

BY LOUIS SATTLER AND F. W. ZERBAN

The Dreywood<sup>1</sup> anthrone reagent gives a positive qualitative test for a large variety of carbohydrates and their derivatives, as well as for furfural and 5-hydroxymethylfurfural, but it gives a negative test<sup>2</sup> for D-glucose phenylosazone and D-glucose phenylosotriazole. In view of the fact that a positive test is obtained with D-mannose phenylhydrazones, the writers<sup>3</sup> suggested that the anthrone reaction requires the initial formation of furfural or a derivative of it.

In the mechanism of the formation of 5-hydroxymethylfurfural from sugars, Wolfrom, Schuetz and Cavalieri<sup>3</sup> proved that the first step requires the elimination of a molecule of water between carbons 2 and 3, leaving an OH group on carbon 2. The anthrone test has now been applied to D-glucosone<sup>4</sup> and to 2-desoxyribose<sup>5</sup> and in each case the expected negative test was observed, thus supporting the original postulation for the requirement for a positive test. With 5-desoxy-L-sorbose<sup>6</sup> a non-characteristic tan to lavender color was obtained depending on the sugar concentration.

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- (1) Dreywood, *Ind. Eng. Chem., Anal. Ed.*, **18**, 499 (1946).
- (2) Sattler and Zerban, *Science*, **108**, 207 (1948).
- (3) Wolfrom, Schuetz and Cavalieri, *THIS JOURNAL*, **70**, 514 (1948).
- (4) Becker and May, *ibid.*, **71**, 1491 (1949).
- (5) Sowden, *ibid.*, **72**, 808 (1950).
- (6) Regna, *ibid.*, **69**, 246 (1947).

BROOKLYN COLLEGE  
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### A Synthesis of N,N-Diphenylcarbamic Anhydride<sup>1</sup>

BY W. A. SCHROEDER AND PHILIP E. WILCOX

The only reported synthesis of N,N-diphenylcarbamic anhydride is that of Herzog and Budy<sup>2</sup> who prepared it by treating the addition product of pyridine and N,N-diphenylcarbonyl chloride with dilute sodium hydroxide. Since their procedure failed to give satisfactory results, recourse was had to a classical method for the preparation

- (1) This paper is based on work done for the Office of Scientific Research and Development under Contract OBMsr-381 with the California Institute of Technology.
- (2) J. Herzog and K. Budy, *Ber.*, **44**, 1584 (1911).