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.[4] 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.[5] 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_{HAc} 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

BY JOHN R. SAMPEY AND ANNE K. MCCUEN

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.[1] *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.[2] *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.).[3]

Acknowledgment.—The authors acknowledge the interest of Dr. E. Emmet Reid in this research. The work was done under Contract N7onr-381 with the Office of Naval Research.

[1] Sampey, Blitch and King, THIS JOURNAL, **70**, 2606 (1948).

[2] Sampey, Fawcett and Morehead, *ibid.*, **62**, 1839 (1940).

[3] Shoesmith 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[1] 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[2] for D-glucose phenylosazone and D-glucose phenylosotriazole. In view of the fact that a positive test is obtained with D-mannose phenylhydrazone, the writers[2] 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[3] 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[4] and to 2-desoxyribose[5] 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[6] a non-characteristic tan to lavender color was obtained depending on the sugar concentration.

The writers wish to thank Clarence E. May of Indiana University, John C. Sowden of Washington University and Peter P. Regna of Charles Pfizer and Company, for their kind coöperation.

[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).

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A Synthesis of N,N-Diphenylcarbamic Anhydride[1]

BY W. A. SCHROEDER AND PHILIP E. WILCOX

The only reported synthesis of N,N-diphenylcarbamic anhydride is that of Herzog and Budy[2] who prepared it by treating the addition product of pyridine and N,N-diphenylcarbamyl 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 OEMsr-881 with the California Institute of Technology.

[2] J. Herzog and K. Budy, *Ber.*, **44**, 1584 (1911).

of acid anhydrides and it was possible to prepare the compound by the reaction of potassium N,N-diphenylcarbamate and N,N-diphenylcarbamyl chloride. This product differed from that of Herzog and Budy and the difference seems to lie in the fact that their material was a complex of two molecules of anhydride with one of diphenylamine. Because only a small amount of pure material was required for our purposes, no attempt was made to refine the procedures which are described below.

Experimental Part

Stem corrections were applied to melting points all of which were taken in melting point tubes in an electrically heated copper block.

Potassium N,N-Diphenylcarbamate (I).—The method of preparation was essentially that of Heussermann.[3] An 8.3-g. sample of potassium was added to 100 g. of molten diphenylamine (Eastman Kodak Co. White Label recrystallized) at 90°. After the first vigorous reaction had ceased, the flask was evacuated and heating at 120° was continued for five and one-half hours in order to complete solution of the potassium. A heavy yellow sand-like precipitate settled in the molten diphenylamine. Excess diphenylamine was dissolved by adding 200 ml. of anhydrous ether to the cooled mixture. When carbon dioxide was bubbled through the suspension, the sandy precipitate was replaced by a loose, fine, white powder. The powder was centrifuged, washed seven times with 150-ml. portions of anhydrous ether to remove diphenylamine, and dried. The yield was 55 g. of nearly white powder. Analysis showed that the crude material was far from pure but since the impurity was probably potassium carbonate, purification was not attempted.

N,N-Diphenylcarbamic Anhydride.—About 50 g. of (I) and 40 g. of N,N-diphenylcarbamyl chloride (Eastman White Label recrystallized) were mixed and heated in an oil-bath at 90°. After fifteen minutes, the melt had become a grey paste. The heating was continued for five hours with frequent stirring. Throughout this time, the melt did not change in color but did bubble slightly. When the cooled paste was digested with 150 ml. of boiling methanol, much material dissolved. After the insoluble portion had been centrifuged from the dark red-brown solution, about 30 g. of yellowish crystalline material slowly formed in the solution on cooling in an ice-salt-bath. Recrystallization from methanol resulted only in the formation of 16 g. of material which was more highly colored than the crude product but when this dark-colored material was recrystallized twice in small portions from boiling acetone (2.5 ml. per g.) and once from methanol, 5.5 g. of greyish-yellow crystals were formed which melted at 121.5–122.5° in good agreement with the melting point of 122–123° which is recorded by Herzog and Budy.[2] The analysis, however, indicated that the material was a complex of two molecules of anhydride and one of diphenylamine.

Anal. Calcd. for anhydride: C, 76.43; H, 4.95; N, 6.86; mol. wt., 408. Calcd. for complex: C, 77.93; H, 5.23; N, 7.10; mol. wt., 986 (3 × 329). Found: C, 77.89, 77.69; H, 5.01, 4.94; N, 7.06, 7.38; mol. wt., 321, 329 (Rast micromethod in exaltone).

Experiments showed that recrystallization from absolute ethanol which contained hydrogen chloride yielded a product of melting point of about 129°. Accordingly, 4 g. of the complex was dissolved in 30 ml. of hot absolute ethanol and hydrogen chloride gas was passed into the solution. Cooling of the solution produced fairly large colorless prisms. By repeated crystallization from ethanol–hydrogen chloride and finally from ethanol, a product was finally obtained which melted at 128.5–130°. The following analyses were obtained.

Anal. Calcd. for $C_{26}H_{20}O_3N_2$: C, 76.43; H, 4.95; N, 6.86; mol. wt., 408. Found: C, 76.68, 76.55; H, 4.73, 4.80; N, 7.18, 7.12; mol. wt., 402 (Rast micromethod in exaltone).

Probably the purification could be much improved if the methanolic extract of the reaction mixture were saturated with hydrogen chloride before the product is first crystallized. Several recrystallizations, of which the last should be from ethanol in order to remove traces of hydrogen chloride, should then yield a pure product. The use of hydrogen chloride is effective because the hydrochloride of diphenylamine is stable and soluble in methanol or ethanol.

Proof of Structure of N,N-Diphenylcarbamic Anhydride.—The material of Herzog and Budy[2] probably was the complex of N,N-diphenylcarbamic anhydride and diphenylamine although their analyses, especially for carbon, were not unsatisfactory. However, the compound which was prepared in the present study and which melts at 128.5–130° may be shown to be the anhydride itself on the basis of the following facts.

(1) The analyses and molecular weight agree with the calculated composition and molecular weight of the anhydride.

(2) Ammonolysis yielded 80% of the N,N-diphenylurea (proved by mixed melting point with an authentic sample) which should be formed if 2 moles of ammonia react to form one mole of N,N-diphenylurea and one mole of ammonium diphenylcarbamate. Herzog and Budy also carried out this reaction which by itself is a poor proof of structure.

(3) Hydrolysis with refluxing *N* sodium hydroxide for forty-eight hours produced 90% of the theoretical diphenylamine if it is assumed that one mole of anhydride is hydrolyzed to 2 moles of diphenylamine. In this procedure, the diphenylamine was extracted from the hydrolysate with ether and the quantity was determined by chromatographic-spectrophotometric methods.[4]

(4) Compounds such as diphenyloxanilide, tetraphenylurea, methyl or ethyl N,N-diphenylcarbamate which might be formed during the reaction or purification are excluded on the basis of melting point.

Some Properties of the Anhydride.—N,N-Diphenylcarbamic anhydride is very soluble in chloroform, soluble in benzene, acetone, ethanol, and warm methanol, and slightly soluble in ligroin, ethyl ether, and cold methanol. It can be heated in ethanol or methanol without change and much can be recovered unchanged after refluxing for two hours in ethanol which contains potassium ethoxide. Norite causes decomposition in hot alcoholic solution.

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(3) C. Heussermann, *J. prakt. Chem.*, **58**, 367 (1898).

(4) W. A. Schroeder, E. W. Malmberg, L. L. Fong, K. N. Trueblood, J. D. Landerl and E. Hoerger, *Ind. Eng. Chem.* **41**, 2818 (1949).

The Synthesis of 1-Methylcyclopropanemethanol

BY SAMUEL SIEGEL AND CLARENCE G. BERGSTROM

As a prelude to a kinetic investigation of the chemical effects of the cyclopropyl group, the previously unknown 1-methylcyclopropanemethanol has been synthesized. Paralleling the work of von Auwers[1] on the thermal decomposition of the pyrazoline resulting from the reaction of diazomethane and ethyl methacrylate, we have found that the corresponding pyrazoline resulting from the reaction of diazomethane and methyl methacrylate gives a mixture of 70%

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(1) von Auwers and Konig, *Ann.*, **496**, 27, 252 (1932).