above. Five minutes were allowed for the establishment of thermal equilibrium, and the length of the emergent stem of the floating hydrometer was then measured. The density of the liquid fluorine, calculated from a two-constant interpolation formula, was 1.56 g./cc. The reading did not change with time, nor after agitation. As a further verification of the accuracy of the hydrometer, it was removed from the apparatus and placed in a phosphoric acid solution of such concentration that the hydrometer floated at the same level as in the liquid fluorine; the density of this solution as determined in a pycnometer was 1.554 g./cc. The sensitivity of the hydrometer in the density range of interest was determined to be 0.008 g./cc. for a millimeter change in emergent stem length.

After the application of a 1% correction for the difference between the surface tensions of the fluorine and the calibration liquids, and assuming a possible uncertainty in the cathetometer reading of ±1 mm., the density of liquid fluorine at −196° was computed to be 1.54 g./cc. with an estimated uncertainty of 0.02 g./cc.

A second sample of fluorine from a cylinder which had been stored for approximately one year, and hence presumably was not from the same lot, was analyzed as 98.6% pure by the method of Kimball and Tufts.[3] This sample gave values of the density identical with that reported above.

A third sample of fluorine was condensed directly from an electrolytic cell after passage over potassium fluoride pellets to remove the major portion of the hydrogen fluoride. The density, measured with a smaller hydrometer and with less precision than before, was found, after a 2% correction for surface tension effects, to be 1.51 ± 0.04 g./cc.

It was observed that a white flocculent precipitate was present in all the samples of liquefied fluorine. This material was volatile at room temperature, hence it may have been hydrogen fluoride. The flocculent solid had no apparent effect upon the hydrometer readings inasmuch as the same readings were obtained before and after careful stirring to dislodge precipitate which had settled on the hydrometer bulb.

Acknowledgment.—The financial support of this work by the Office of Naval Research is gratefully acknowledged. The authors also wish to thank Mr. J. B. Hatcher of the Jet Propulsion Laboratory, California Institute of Technology, for assistance with portions of this work.

---

[3] R. H. Kimball and L. E. Tufts, "Complete Analysis of Fluorine Gas," MDDC 195, Atomic Energy Commission, 1946.

RESEARCH DIVISION
AEROJET ENGINEERING CORPORATION
AZUSA, CALIFORNIA
RECEIVED AUGUST 6, 1951

Preparation of 2-Methyl-5-*t*-butyl-3-carbethoxyfuran during the Hydrolysis of Ethyl α-Pinacolonylacetoacetate

BY NICHOLAS MESSINA AND ELLIS V. BROWN

During the course of our investigation of the Friedel–Crafts reaction in the thiophene series,[1] it became necessary to prepare 6,6-dimethylheptanedione-2,5 by the hydrolysis and decarboxylation of ethyl α-pinacolonylacetoacetate. The hydrolysis of this substituted ethyl acetoacetate gave some unexpected results when the hydrolyzing agent was boiling 20% potassium carbonate solution. Youtz and Perkins[2] have shown that the above-mentioned reagent could be used to prepare 3-methylacetonylacetone from ethyl α,β-diacetylbutyric ester. Hughes and co-workers[3] employed a similar procedure to prepare heptanedione-2,5 from ethyl α-acetyl-β-propionylpropionate. Rodionov[4] prepared acetonylacetone from ethyl α-acetylacetoacetate by this method. When 20% potassium carbonate solution was used in the hydrolysis of ethyl α-pinacolonylacetoacetate, 2-methyl-5-*t*-butyl-3-carbethoxyfuran was produced. The structure of this ester was established by alkylating the known 2-methyl-3-carbethoxyfuran[5] with *t*-butyl chloride according to the method of Gilman.[6] The resulting ester and that obtained by ring closure with potassium carbonate were hydrolyzed to the corresponding acid (2-methyl-5-*t*-butyl-3-furancarboxylic acid). A mixture of the two samples showed no depression of melting point.

Experimental

2-Methyl-5-*t*-butyl-3-carbethoxyfuran.—Ninety-nine grams (0.43 mole) of ethyl α-pinacolonylacetoacetate was refluxed for six hours with a solution containing 80 g. of potassium carbonate in 320 ml. of water. After cooling, the reaction mixture was extracted with ether, washed with water and dried over anhydrous sodium sulfate. Rectification yielded 54 g. (60%) of 2-methyl-5-*t*-butyl-3-carbethoxyfuran, b.p. 75–77° (1 mm.).

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.57; H, 8.57. Found: C, 68.41; H, 8.69.

Hydrolysis of the furan ester with 15% aqueous potassium hydroxide resulted in 2-methyl-5-*t*-butyl-3-furancarboxylic acid, m.p. 95°, after crystallization from alcohol–water.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.93; H, 7.69. Found: C, 66.14; H, 7.84.

2-Methyl-5-*t*-butyl-3-furancarboxylic Acid by Friedel–Crafts Reaction.—2-Methyl-3-carbethoxyfuran, 15.4 g. (0.1 mole) and 13.7 g. (0.1 mole) of *t*-butyl bromide were added dropwise over a 25-minute period to 19.1 g. (0.15 mole) of aluminum chloride and 200 ml. of carbon disulfide contained in a three-necked flask cooled by an ice-bath. A dark viscous mass separated making stirring impossible. When the addition was complete, the ice-bath was removed and the mixture allowed to stand for 24 hours. The reaction product was poured on cracked ice with vigorous stirring, the solvent separated, and the aqueous layer extracted with ether. The ether and carbon disulfide solutions were combined, washed with water, 10% sodium carbonate and dried over sodium sulfate. Fractionation yielded 13.4 g. (54%) of 2-methyl-5-*t*-butyl-3-carbethoxyfuran, b.p. 80–81° (2 mm.).

Ten grams (0.04 mole) of 2-methyl-5-*t*-butyl-3-carbethoxyfuran was refluxed with a 15% aqueous solution of potassium hydroxide. Isolation of the acid in the usual manner yielded, after recrystallization from an alcohol–water mixture, 7.5 g. (85%) of 2-methyl-5-*t*-butylfuran-3-carboxylic acid, m.p. 95°. A mixed melting point with a sample obtained from the hydrolysis of the ester derived from ethyl α-pinacolonylacetoacetate showed no depression.

Anal. Calcd. for $C_{10}H_4O_3$: C, 65.93; H, 7.69. Found: C, 66.20; H, 7.65.

---

[1] N. Messina and E. V. Brown, THIS JOURNAL, **74**, 920 (1952).

[2] M. A. Youtz and P. P. Perkins, *ibid.*, **51**, 3511 (1929).

[3] G. K. Hughes, F. Lions, J. J. Maunsell and T. Wilkinson, *Proc. Roy. Soc. N. S. Wales*, **71**, 406 (1938).

[4] V. M. Rodionov and E. F. Polunina, *Doklady Akad. Nauk S. S. S. R.*, **68**, 535 (1949); *C. A.*, **44**, 1030 (1950).

[5] H. Gilman, R. R. Burtner and E. W. Smith, *Rec. trav. chim.*, **51**, 407 (1932).

[6] H. Gilman and N. O. Calloway, THIS JOURNAL, **55**, 4197 (1933).

CHEMISTRY DEPARTMENT
FORDHAM UNIVERSITY
NEW YORK 58, N. Y.
RECEIVED AUGUST 1, 1951

Additional *o*-Phenylenediamines Tested for Vitamin B_{12} Activity

BY JOHN P. LAMBOOY AND EDWARD E. HALEY

Since the discovery of the presence of 5,6-dimethylbenzimidazole in acid hydrolysates of