The mixture was extracted with chloroform and the dried extract was evaporated to a small volume. Addition of petroleum ether caused the ester to crystallize. The yield was 71% of white powder readily soluble in chloroform or alcohol, sparingly soluble in ether or cold water and insoluble in petroleum ether. A sample was recrystallized from water; m.p. 151–152°.

Anal. Calcd. for $C_9H_{12}N_2O_4$: C, 50.94; H, 5.70; N, 13.21. Found: C, 51.21; H, 5.87; N, 13.47.

Dimethyl 1-Methyl-2-mercapto-4,5-imidazoledicarboxylate.—This was prepared by the condensation of methyl oxalate with N-formylsarcosine methyl ester[2] using sodium methylate, followed by treatment of the aqueous solution of the product with thiocyanic acid. The procedure was essentially the same as that described above for the preparation of diethyl 2-mercapto-4,5-imidazoledicarboxylate. The product was obtained as a finely divided, white, crystalline precipitate in a yield of 70% based on the formylsarcosine ester. A sample for analysis was recrystallized from ethyl acetate containing a little methanol. It separated as fine white needles; m.p. 173.5–174° (uncor.).

Anal. Calcd. for $C_8H_{10}N_2O_4S$: C, 41.73; H, 4.38; N, 12.17. Found: C, 41.52; H, 4.69; N, 12.62.

Dimethyl 1-Methyl-4,5-imidazoledicarboxylate and 1-Methyl-4,5-imidazoledicarboxylic Acid.—To a solution of 20 ml. of concentrated nitric acid in 60 ml. of water was added a few crystals of sodium nitrite and then 23 g. of dimethyl 1-methyl-2-mercapto-4,5-imidazoledicarboxylate was added in small portions with stirring. The mixture was cooled in an ice-bath to keep the temperature at 30–40°. After the reaction was complete the resulting clear solution was chilled to 10°, and a white crystalline solid separated. This was the nitrate salt of dimethyl 1-methyl-4,5-imidazoledicarboxylate. It was collected on a filter and air-dried. The yield was 17 g. (65%). It was readily soluble in water, alcohol or acetone. A sample for analysis was recrystallized from a little water; m.p. 154–155°.

Anal. Calcd. for $C_8H_{10}N_2O_4 \cdot HNO_3$: C, 36.79; H, 4.25; N, 16.09. Found: C, 36.94; H, 4,57; N, 15.63.

The 17 g. of nitrate salt was dissolved in 30 ml. of water and an excess of sodium carbonate was added. An oily layer separated to the top, but it was only sparingly soluble in ethyl acetate or chloroform. The mixture was extracted with two 150-ml. portions of ethyl acetate. This extract was dried and evaporated leaving a colorless oil which crystallized after cooling for several hours. The yield of dimethyl 1-methyl-4,5-imidazoledicarboxylate was 10 g. (77% based on the nitrate salt). The compound was readily soluble in benzene, ethyl acetate or water from which it would not separate again on cooling. A sample was recrystallized from benzene-petroleum ether; m.p. 46.5–47°.

Anal. Calcd. for $C_8H_{10}N_2O_4$: N, 14.14. Found: N, 13.98.

The above aqueous sodium carbonate solution and the original nitric acid filtrate, from which the nitrate salt was obtained, were combined, made basic with sodium hydroxide solution and heated to boiling. After cooling, the solution was acidified to *p*H 2 with hydrochloric acid and chilled in the ice-box. The white crystalline precipitate of 1-methyl-4,5-imidazoledicarboxylic acid which separated was collected on a filter, washed with a little ice-water and air-dried. The yield was 7.5 g. (44% based on the original dimethyl 1-methyl-2-mercapto-4,5-imidazoledicarboxylate). A sample was recrystallized from water and separated as fine, lustrous needles, m.p. 261–262° dec. (uncor.).

Anal. Calcd. for $C_6H_6N_2O_4$: C, 42.36; H, 3.56. Found: C, 42.52; H, 4.01.

Diethyl 1-Phenyl-2-mercapto-4,5-imidazoledicarboxylate.—This was prepared by the same procedure as described above for the preparation of diethyl 2-mercapto-4,5-imidazoledicarboxylate, using N-formyl-N-phenylglycine ethyl ester[2] in place of N-formylglycine ethyl ester. In the condensation with thiocyanic acid, an equal volume of alcohol was added to the water solution in order to maintain homogeneity. At the end of the reaction the mixture was evaporated under reduced pressure to remove most of the alcohol. The product was obtained as a brown crystalline solid which was collected on a filter, washed well with water and air-dried. The yield was 86%. A sample was recrystallized from alcohol; m.p. 146–147°.

Anal. Calcd. for $C_{15}H_{16}N_2O_4S$: C, 56.25; H, 5.00; N, 8.74. Found: C, 56.30; H, 5.43; N, 8.74.

1-Phenyl-2-mercapto-4,5-imidazoledicarboxylic Acid.—The above ester, 12 g., was saponified with 6 *N* sodium hydroxide solution. Acidification of the solution with a large excess of concentrated hydrochloric acid caused precipitation of a yellow solid. This was collected and taken up in 100 ml. of warm acetone. The acetone solution was filtered from some sodium chloride which was present, and evaporated under reduced pressure. The crystalline residue, 8 g., dissolved readily in 150 ml. of cold water. To this solution was added 100 ml. of concentrated hydrochloric acid which caused immediate precipitation of the 1-phenyl-2-mercapto-4,5-imidazoledicarboxylic acid as a crystalline solid; m.p. 200–201° dec.; yield 7.8 g. (74%).

Anal. Calcd. for $C_{11}H_8N_2O_4S$: N, 9.93; neut. equiv., 141.1. Found: N, 9.94; neut. equiv., 141.2.

1-Phenyl-4,5-imidazoledicarboxylic Acid and Esters.—The above diethyl 1-phenyl-2-mercapto-4,5-imidazoledicarboxylate was oxidized with dilute nitric acid and the mixture worked up as described above for the preparation of diethyl 4,5-imidazoledicarboxylate. The product, diethyl 1-phenyl-4,5-imidazoledicarboxylate, was obtained as a brown oil which eventually crystallized. The yield was 80%. A sample was recrystallized from ethyl acetate-petroleum ether mixture; m.p. 84–85°.

Anal. Calcd. for $C_{15}H_{16}N_2O_4$: C, 62.49; H, 5.60; N, 9.72. Found: C, 62.40; H, 5.61; N, 10.03.

1-Phenyl-4,5-imidazoledicarboxylic acid obtained by saponification of the diethyl ester was recrystallized from water; m.p. 199–200° dec.

Anal. Calcd. for $C_{11}H_8N_2O_4$: C, 56.80; H, 3.43. Found: C, 56.84; H, 3.80.

Dimethyl 1-phenyl-4,5-imidazoledicarboxylate, obtained by esterification of the acid with methanol and hydrogen chloride, melted at 86–87° after recrystallization from alcohol.

Anal. Calcd. for $C_{13}H_{12}N_2O_4$: N, 10.77. Found: N, 10.88.

THE LILLY RESEARCH LABORATORIES
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The Density of Liquid Fluorine

BY SCOTT B. KILNER, CARL L. RANDOLPH, JR., AND ROLLIN W. GILLESPIE

Kanda[1] has reported values of the density of liquid fluorine in the temperature range −216° to −188°. The density at −196°, determined from these results, is 1.13 g./cc. We have recently redetermined the density of liquid fluorine at this temperature and have found a value of 1.54 ± 0.02 g./cc.; Kanda's result therefore appears to be in error by approximately 27%.

A hydrometer, so proportioned as to cover the density range from 1.05 to 1.60 g./cc. in a stem length of 20 cm., was constructed from Pyrex glass, and was calibrated at room temperature in solutions of known density. On the assumption that the thermal coefficient of expansion of Pyrex glass is 1×10^{-5} $°C.^{-1}$, the change of temperature would have necessitated a correction of only 0.2%, hence it was ignored. The hydrometer was enclosed in a Pyrex tube fitted with inlets for flushing and for blanketing with helium, and for the introduction of fluorine. Fluorine could be condensed in this apparatus after it had been immersed in a large unsilvered dewar flask containing liquid nitrogen. The length of the emergent stem of the hydrometer could then be measured visually with a cathetometer. The accuracy of the calibration at low temperatures was verified by the determination of the density of liquid oxygen at −196° as 1.18 ± 0.02 g./cc. (literature value, 1.20 g./cc.[2]).

Fluorine, obtained from the Pennsylvania Salt Manufacturing Company, was liquefied in the apparatus described

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(1) E. Kanda, *Bull. Chem. Soc., Japan,* **12**, 469, 473 (1937).

(2) "Int. Crit. Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1927.

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.

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

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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.

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

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[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).

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

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