run. Improvement might have been effected by the use of coated ribbons to increase the area pyrometered.

At temperatures above 2400°K., relatively large losses of tungsten were noted. These losses were more than could be accounted for by evaporation, and were assumed to be the result of a reaction between thorium oxide and tungsten in which volatile tungsten oxides were formed.

Acknowledgment.—Mr. F. H. Morgan's help in obtaining the calibration curve with the W–Mo thermocouple and Mr. H. Bleecher's technical assistance are gratefully acknowledged.

BARTOL RESEARCH FOUNDATION
OF THE FRANKLIN INSTITUTE
SWARTHMORE, PENNSYLVANIA

Ethyl β-Morpholinocrotonate

BY J. F. TINKER AND T. E. WHATMOUGH

RECEIVED JUNE 9, 1952

Monoalkylation of acetoacetic ester is seldom clean and sometimes difficult. Alkylation of β-aminocrotonic ester[1] stops cleanly after a single alkyl group. A most satisfactory member of this series is the one derived from morpholine, using directions for the preparation of β-anilinocrotonate.[2]

Ethyl β-Morpholinocrotonate.—A mixture of 511 g. (3.93 moles) of ethyl acetoacetate, 400 cc. (4.60 moles) of morpholine, 10 cc. of 85% formic acid, and 2.5 l. of benzene was refluxed, and the water separated.[2] In 8 hours 75 cc. had been collected. The solution was then distilled, and yielded 592 g., 76%, of the product, b.p. 120–124° (0.5 mm.), d^{25}_{25} 1.099, $n^{23.5}_{D}$ 1.5162. A sample was redistilled (b.p. 116° (0.35 mm.)) and analyzed.

Anal. Calcd. for $C_{10}H_{17}NO_3$ (199.24): C, 60.28; H, 8.60. Found: C, 60.20; H, 8.65.

Treatment of the aminoester with either propargyl bromide or propargyl *p*-toluenesulfonate, followed by treatment with hot water,[1] yielded **3-carbethoxy-5-hexynone-2**, b.p. 69–73° (1 mm.), in excellent yield. A single redistillation gave a sample of analytical purity (b.p. 71° (1 mm.)).

Anal. Calcd. for $C_9H_{12}O_3$ (168.19): C, 64.27; H, 7.19. Found: C, 63.60; H, 7.20.

3-Carbethoxy-5-hexynone-2, 2,4-dinitrophenylhydrazone, m.p. 97–98°.[3]

Anal. Calcd. for $C_{15}H_{16}N_4O_3$ (348.31): C, 51.72; H, 4.63; N, 16.09. Found: C, 51.74; H, 4.69; N, 15.94.

Acid hydrolysis yields **5-hexynone-2**,[4] b.p. 62–64° (12 mm.). The **2,4-dinitrophenylhydrazone** of **5-hexynone-2** melts at 138–139°.

Anal. Calcd. for $C_{12}H_{12}N_4O_4$ (276.25): N, 20.28. Found: N, 20.34.

Treatment of ethyl β-morpholinocrotonate with 2,3-dichloropropene, followed by refluxing with water, yielded directly **5-chloro-5-hexenone-2**, b.p. 74–77° (16 mm.) in 86% yield. **The 2,4-dinitrophenylhydrazone** has m.p. 84–85°.

Anal. Calcd. for $C_{12}H_{13}ClN_4O_4$ (312.71): C, 46.09; H, 4.19; N, 17.92. Found: C, 46.12; H, 4.31; N, 18.34.

Treatment of the chloroketone with sodium amide in liquid ammonia, in an attempt to effect the condensation of two molecules to a derivative of 1,6-cyclodecadiyne, yielded no detectable tertiary alcohol.

Acknowledgment.—We wish to thank Dr. M. C. Whiting for informative discussions during the course of this work.

CONVERSE LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE 38, MASS.

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(1) (a) R. Robinson, *J. Chem. Soc.*, **109**, 1043 (1916); (b) W. M. Lauer and G. W. Jones, THIS JOURNAL, **59**, 232 (1937).

(2) C. S. Hamilton, ed., *Org. Syntheses*, **29**, 42 (1949).

(3) All melting points taken with Anschütz thermometers in a Hershberg apparatus.

(4) T. E. Gardner and W. H. Perkin, *J. Chem. Soc.*, **91**, 851 (1907).

COMMUNICATIONS TO THE EDITOR

THREE NEW NEUTRON DEFICIENT ISOTOPES OF YTTRIUM

Sir:

Three new yttrium isotopes have been discovered by proton bombardment of spectroscopically pure yttrium oxide[1] in the Rochester 130-inch cyclotron. Targets of yttrium oxide were placed in an aluminum foil envelope which was mounted on the end of a probe and placed inside the tank of the cyclotron. The target was bombarded with both 240 and 130 Mev. protons for exposure times of one and two hours.

The yttrium oxide was dissolved in hot nitric acid and inert carriers of zirconium, strontium, rubidium and bromine were added to the solution. The yttrium fraction was purified from all the spallation products and the sample was followed under a Geiger-Müller tube for gross decay. The activities found had half lives of: 2–4 hours, 14 hours, 38 hours, 80 hours, 25.5 days and finally 65 days. In one experiment 105-day Y^{88} was also observed. The half-lives of the known[2] yttrium isotopes in this region are: Y^{88} 2 hours, 105 days; Y^{87} 14 hours, 80 hours; Y^{86} 14.6 hours; and Y^{84} 3.7 hours. The 38-hour, 25.5-day, and 65-day activities found in the yttrium gross decay curve can be identified with Sr^{83}, Sr^{82}, and Sr^{85}, respectively. This means that these strontium isotopes found in the purified yttrium sample are the daughters of their respective yttrium parents which are previously unreported yttrium isotopes. Thus, Y^{82} decayed to 25.5-day Sr^{82}, Y^{83} decayed to 38-hour Sr^{83}, and Y^{85} decayed to 65-day Sr^{85}.

Since the yttrium gross decay curve was so complex, it was impossible to resolve the half lives of these new isotopes directly. Therefore, a series of isolation experiments were performed in which the strontium daughter isotopes were removed from the yttrium at periodic intervals. These strontium

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(1) The yttrium oxide was supplied through the courtesy of Ames Laboratory, Iowa State College.

(2) Nuclear Data by K. Way, *et al.*, Circular of the National Bureau of Standards 499; General Electric Research Laboratory Chart of the Nuclides.

isolations were then followed for decay. The period of growth of the strontium daughters was kept constant during a given run and was usually six hours. A total of six strontium isolations was made. A known amount of strontium carrier was added each time, and the recovery yield was determined. Each sample was mounted in the same manner and counted under both a Geiger–Müller tube and a scintillation counter with constant geometry. The strontium isolations showed the following half lives: 2.8 hours, 38 hours, 25.5 days, and 65 days. The 2.8-hour half life is the Sr^{87} daughter of 14-hour, 80-hour Y^{87}. The yield of each of the strontium daughters was determined by extrapolating the decay curve for each activity to the time of isolation. The radioactivity was then corrected for chemical yield and a plot of corrected yields *vs.* isolation time was made for each of the three strontium isotopes: Sr^{82}, Sr^{83}, and Sr^{85}. The slope of these curves gives the half life of the respective yttrium parents. These experiments give the following values for the half lives of the yttrium isotopes: Y^{82} 70 ± 10 minutes, Y^{83} 3.5 ± 0.5 hours, Y^{85} 5 ± 1 hours.

The genetic relationship of these isotopes with the known strontium daughters has been established in five separate experiments. The total yield of Y^{82} varied with each bombardment and on several occasions the Sr^{82} daughter appeared in only the first isolation decay curve. The investigation of these new yttrium isotopes is being continued in an effort to establish their half lives more accurately and to determine the nature of their radiations.

This work was done under support by the U. S. Atomic Energy Commission. We wish to thank Professor S. W. Barnes and the operating crew of the cyclotron for the bombardments.

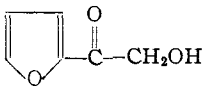
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROCHESTER
ROCHESTER 3, NEW YORK
ALBERT A. CARETTO, JR.
EDWIN O. WIIG

RECEIVED SEPTEMBER 2, 1952

2-HYDROXYACETYLFURAN FROM SUGARS

Sir:

For many years it has been assumed that the dehydration of hexoses, or polysaccharides which contain hexose units, in neutral or acidic aqueous solutions yields only one furan derivative, 5-hydroxymethyl-2-furaldehyde (HMF).[1] While 2-furaldehyde has been observed in certain cases,[2,3,4] it has generally been regarded as a secondary product derived from decomposition of the initially formed HMF.[2,3] We wish to report the isolation of another furan compound, 2-hydroxyacetylfuran (I) (or furoylcarbinol), from the acid-catalyzed dehydration of sucrose and D-glucose in aqueous solutions.



I

We have prepared HMF by essentially the same procedure as that described by Middendorp[3] (25% sucrose solution, 0.7% oxalic acid by weight of sucrose, 140° for three hours, neutralization with lime, extraction with ethyl acetate. Middendorp treated his final neutralized reaction mixture with basic lead acetate before the extraction; we have omitted this step in our preparations). In the course of the purification of the crude HMF by distillation under reduced pressure we observed the appearance of a crystalline material which sublimed on to the walls of the water-cooled condenser, the receiver and even into the Dry Ice trap following the receiver. Subsequent examination of the material demonstrated that it is 2-hydroxyacetylfuran. We estimate on the basis of this separation that the 2-hydroxyacetylfuran represents a minimum of one to two per cent. by weight of the crude HMF. The compound was obtained in like manner from crude HMF obtained by an acid-catalyzed dehydration of D-glucose in aqueous solution. Middendorp appears to have observed the compound during the distillation of crude HMF but assumed that it was HMF.[3]

The 2-hydroxyacetylfuran was purified by recrystallization from benzene or *n*-hexane and by sublimation under reduced pressure (80°/2–3 mm.); m.p. 83–84.5°[5]. *Anal.*[6] Calcd. for $C_6H_6O_3$: mol. wt. 126.1; C, 57.14; H, 4.80. Found: mol. wt., 127, 131; C, 57.06, 57.13; H, 4.90, 4.97. Aqueous solutions of the material exhibit a major absorption maximum at 275 mμ (molar extinction coefficient of 14,000 liters per mole cm.) and a minor absorption maximum at 225 mμ (molar extinction coefficient of 2790 liters per mole cm).[7,8] The compound reduces Fehling solution but gives no coloration with fuchsin–sulfurous acid reagent. Treatment of the 2-hydroxyacetylfuran with benzoyl chloride in pyridine yields a crystalline benzoate which after recrystallization from *n*-hexane melts at 74.5–76°.

Although 2-hydroxyacetylfuran has not been isolated previously from carbohydrate sources it has been prepared by the hydrolysis of 2-diazoacetylfuran.[9] The material, m.p. 81–82°, was found to reduce Fehling solution and to yield a benzoate of m.p. 75.5–76°. No absorption data were reported.

We repeated this latter preparation of 2-hydroxyacetylfuran and obtained a material which melted at 83–85.3°. Mixed m.p. determinations with our compound showed no depression. This 2-hydroxyacetylfuran in aqueous solution exhibits a major

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(1) F. H. Newth, "The Formation of Furan Compounds from Hexoses," "Advances in Carbohydrate Chemistry," Vol. 6, pp. 83–106, Academic Press Inc., New York, N. Y. 1951.

(2) E. Erdmann, *Ber.*, **43**, 2391–2398 (1910).

(3) J. A. Middendorp, *Rec. trav. chim.*, **38**, 1–71 (1919).

(4) T. E. Friedemann and Patricia K. Keegan, "Assay Methods, Chemical and Physiological Properties of Browning Substances in Foods and Their Derivatives in Urine," Report No. 3, September 1, 1949–August 31, 1950, PB 103025, U. S. Department of Commerce, Office of Technical Services, Washington, D. C.

(5) Melting points are uncorrected.

(6) Analyses by Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

(7) HMF in aqueous solution exhibits a major absorption maximum at 284 mμ (molar extinction coefficient 16,700 liters per mole cm.) and a minor absorption maximum at 230 mμ (molar extinction coefficient 3,080 liters per mole cm.) B. Singh, G. R. Dean and S. M. Cantor, THIS JOURNAL, **70**, 517–522 (1948).

(8) We wish to thank J. Devlin of these laboratories for the determination of the spectrophotometric data.

(9) F. Kipnis, H. Soloway and J. Ornfelt, THIS JOURNAL, **70**, 142–143 (1948).