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.

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Ethyl β-Morpholinocrotonate

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

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

(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).

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.

(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).

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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.

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

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

(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.

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            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.

(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.
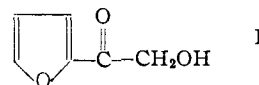
We have prepared HMF by essentially the same procedure as that described by Middendorp[3] (25% sucrose solution, 0.7% oxalic acid by weight of sucrose, 140° for three hours, neutralization with lime, extraction with ethyl acetate. Middendorp treated his final neutralized reaction mixture with basic lead 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

(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).

absorption maximum at 275 mμ (molar extinction coefficient of 13,900 liters per mole cm.) and a minor absorption maximum at 225 mμ (molar extinction coefficient of 2980 liters per mole cm.).

It is not our purpose at this time to attempt any explanation of the mechanism of the formation of 2-hydroxyacetylfuran from sugars. The study of the formation and further decomposition of this compound during the dehydration of sugars is being continued.

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BOOK REVIEWS

Chimie Physique. By GUY EMSCHWILLER, Professeur à l'École Supérieure de Physique et de Chimie Industrielles de Paris. Vol. I, Thermodynamique chimique. Equilibres gazeux. ix + 440 pp., 34 figs. 14 × 19 cm. Price, 1200 fr. Vol. II, Equilibres en solutions. Phénomènes de surface. viii + 480 pp., 64 figs 14 × 19 cm. Price, 1300 fr. Vol. III, Cinétique chimique. Structure des molécules. vii + 533 pp. 70 figs. 14 × 19 cm. Price, 1800 fr. Presses Universitaires de France, 108, Boulevard Saint-Germain, Paris, 1951.

It is a pleasure to welcome this valuable addition to the rather scanty production of French books on Physical Chemistry. Professor Emschwiller has done his students, and more generally all French chemists, a great service in writing this clear, comprehensive and thoroughly modern text. Indeed, for some reason or other physical chemistry has not aroused widespread interest in France until recent years; its position as a distinct entity in the general scheme of sciences was never quite clear to the French mind. For instance, it is stated in the preface: "The reader may wonder why this book was classified in the chemistry section of the Collection rather than in the physics section." It would appear that in most other countries such a question was solved long ago, if it ever came up.

The textbook is divided into three separate volumes, each with its own very detailed table of contents and a list of symbols. The latter do not always have the same meaning in the three volumes which may result in some confusion. The first volume is devoted entirely to chemical thermodynamics; the subject is first introduced from the viewpoint of affinity. This concept, which has fallen into some disrepute because of its vagueness, is used extensively and is even represented by a special symbol. The international nomenclature on thermodynamics is followed in general although there are some notable exceptions, as is befitting. Thus Helmholtz free energy is called F while Gibbs free energy is given the symbol G. . . and a new name: "Free Enthalpy." Throughout that section the treatment is rigorous without being too formal. The notions of thermodynamic potential, fugacity and activity are used after the method of Lewis and Randall. Gaseous equilibria then take up the next eight chapters. Several industrially important reactions are considered in detail as an application of general principles. The problem of specific heats is the occasion for introducing statistical thermodynamics which is then developed adequately in the last six chapters.

Volume II is divided into two main parts of nearly equal lengths: equilibria in solutions and surface chemistry. Phase equilibria are not presented as a whole in the usual fashion; instead, one-component systems are considered in a special chapter on first- and second-order transformations (in Vol. I) while two-component systems come up in connection with the colligative properties of solutions. After the classical treatment of electrochemical cells the Debye-Hückel theory is presented followed by Bronsted's theory of acids.

Colloid chemistry comprises a first section on surface phenomena and two chapters on preparation and properties of colloidal solutions. The section closes with an interesting discussion of the various methods used for particle size determination.

In the first half of Vol. III chemical kinetics are dealt with in 10 chapters extending over some 200 pages. After an outline of the fundamentals such topics as free radicals and chain reactions, explosions, electrochemical, photochemical and liquid phase reactions are discussed adequately. The second part, concerning molecular structure, is that which interested the reviewer most and which, no doubt, will prove the more useful to French chemists because of the lack of other texts on the same subject. First the Bohr–Sommerfeld theory of the atom is exposed and then the most recent views on the chemical bond. The quantum theory of valence is outlined in a non-mathematical manner, after the bond orbital and the electron pair methods. Resonance is here called "Mésomerie," but otherwise the treatment follows generally along the lines of Pauling's and similar books. One could wish for a greater number of examples than are discussed in that section. After one chapter each on molecular spectra, magnetochemistry, dipole moments and diffraction methods the book concludes with a last one on the metallic bond. The author and subject index seems quite complete but, unfortunately, it is given only at the end of the third volume. Its usefulness is therefore limited.

One notable difference between this text and English ones is the absence of the three conventional chapters on gases, liquids and solids. Most of the subjects normally covered in those are inserted here and there either in thermodynamics or in molecular structure. Others, such as viscosity of liquids, are missing altogether. The reason for this is possibly that in the French curriculum these topics are considered as relevant of the physics course. Nonetheless it does seem strange not to find at least a brief outline of the kinetic theory of matter in a text book on physical chemistry. On the other hand a particularly commendable feature of Professor Emschwiller's composition is the attention given to what might be termed the "philosophy" of physical chemistry. This is achieved through short historical notes and pertinent considerations on the importance of each subject, its implications and logical relation to the whole.

The physical presentation is appropriately described in the preface as "modest." The format is more suggestive of the typical French novel than of a textbook on science, which makes it somewhat awkward to handle. Translated into dollars the price should hover around $18.00 for the complete work. By comparison with corresponding English textbooks (such as Glasstone's?) this seems a little high, specially considering that, true to the French custom, the three volumes are paper-bound.

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Cottrell: Samaritan of Science. By FRANK CAMERON. Doubleday and Company, Inc., Garden City, New York. 1952. 414 pp. 14 × 21 cm. Price, $4.50.

Cottrell died on November 16, 1948, less than four years ago. It might be thought that his impact on his time and his environment could have been more adequately appraised in a biography written perhaps forty, rather than four years after his death. This may be true, but such a conclusion overlooks the importance of recording promptly the