correct to compare heat of adsorption data with adsorption data plotted according to equation 8 of Walker and Zettlemoyer.[4]

Beebe, *et al.*,[3] indicated the Anderson monolayer volume at a smaller value than the B. E. T. monolayer, thus making Anderson's modification appear to be in the wrong direction. It is true that for a given amount adsorbed, the numerical value of V/V_m from Anderson's equation will be smaller than from the B. E. T. equation, but for this very reason, if the point where Anderson's V/V_m is unity is marked off on a scale graduated in terms of B. E. T.'s V/V_m, it must fall at a place where the graduation shows B. E. T.'s V/V_m to be greater than unity.

These facts support Anderson's equation 6. However, in deriving his equation 17,[2] he has used an expression (equations 13 and 15) for the volume adsorbed in the *n*th layer, V_n, which holds only for the simple B. E. T.[5] model. The appropriate expression for Anderson's model instead of his equation 15, is given by

$$V_n = \frac{V_m c j^{n-1} x^n}{1 + (c - j)x}$$

This, when summed for values of n from 1 to ∞, gives an isotherm equation which is identical with the one obtained by a more direct method in a later publication,[6] as it must since the two equations are deduced from identical postulates.

(4) W. C. Walker and A. C. Zettlemoyer, *J. Phys. Coll. Chem.*, **52**, 47 (1948).

(5) S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938).

(6) R. B. Anderson and W. K. Hall, THIS JOURNAL, **70**, 1727 (1948).

NATIONAL RESEARCH LABORATORIES
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Furan-2-glyoxal

BY FRANK KIPNIS[1] AND JOHN ORNFELT

During work on the synthesis of polycarbonyl compounds, it became desirable to prepare the hitherto unknown furan-2-glyoxal. Several approaches were considered, and two were investigated. The first required the preparation of 2-acetylfuran, followed by oxidation of the ketone with selenium dioxide[1a] to the glyoxal. The second procedure involved the preparation of 2-diazoacetylfuran from furoyl chloride and diazomethane, followed by interaction with hydrogen chloride to give 2-chloroacetylfuran,[2] treatment with pyridine to yield the pyridinium chloride, transformation to the nitrone with *p*-nitrosodimethylaniline and, finally, acid hydrolysis to the glyoxal hydrate.[3]

Until the recent work of Hartough and Kosak[4] on the catalytic acetylation of furan with acetic anhydride and hydriodic acid, the preparation of adequate amounts of 2-acetylfuran was a rather difficult problem. Previously, it had been synthesized by the hydrolysis of ethyl furoylacetate,[5,6,7] from furan, acetyl chloride[8] or acetic anhydride[9] and stannic chloride, from 2-chloromercurifuran and ketene,[10] and from 2-cyanofuran and methylmagnesium iodide.[11]

In the present work which was originated before the disclosures of Hartough and Kosak,[4] the method of the Russian workers[9] was first studied. Their high yields could not be duplicated, much of the furan being lost by resinification. Attention was directed therefore, to treatment of the readily, available furoyl chloride with dimethylcadmium.[12a,b] This reaction gave 2-acetylfuran in 28% yield and was used routinely until displaced by the simpler catalytic technique. Oxidation of the ketone with selenium dioxide went smoothly, and furan glyoxal was isolated in 47% yield.

The Kröhnke-Börner method proceeded as anticipated and furan glyoxal hydrate was isolated in about 11% over-all yield from furoyl chloride, the most severe losses being encountered in the purification of the pyridinium salt. It is not improbable that the yield could be increased considerably by eliminating rigid purification procedures at each step.

Furan-2-glyoxal is a yellow oil with a piercing aroma, develops a green-blue coloration with a mixture of acetic anhydride and sulfuric acid, dissolves in saturated sodium bisulfite with generation of heat, forms a crystalline hydrate on treatment with water, and gives a mono-semicarbazone on interaction with a molar quantity of semicarbazide.

Experimental

2-Acetylfuran. (a) **From Furan and Acetic Anhydride.**—The method of Hartough and Kosak[4] was followed but it was found desirable to add the hydriodic acid at −10° instead of 0°. This modification seemed to aid in the control of the subsequent exothermic reaction.

(b) **From Furoyl Chloride and Dimethylcadmium.**—The Grignard reagent was prepared in a nitrogen atmosphere from 7.4 g. (0.304 mole) of magnesium turnings and 42.5 g. (0.3 mole) of methyl iodide in 200 ml. of anhydrous ether. The dimethylcadmium was made by the addition of 29.4 g. (0.16 mole) of dry cadmium chloride according to the directions of Cason.[12] To the organometallic solution in benzene was added at room tempera-

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(1) Present address: Oxford Products, Inc., Cleveland, Ohio.

(1a) Riley and Gray, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 509.

(2) Burger, U. S. Patent 2,400,913, May 28, 1946; Burger and Harnest, THIS JOURNAL, **65**, 2382 (1943).

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(10) Chute, Orchard and Wright, *J. Org. Chem.*, **6**, 157 (1941).

(11) Asahima and Murayama, *Arch. Pharm.*, **252**, 443 (1914).

(12) (a) Cason and Prout, THIS JOURNAL, **66**, 46 (1944); Cason, *ibid.*, **68**, 2078 (1946); (b) Gilman and Nelson [*Rec. trav. chim.*, **55**, 518 (1936)] prepared propionylfuran from furoyl chloride and diethyl cadmium.

ture 34.2 g. (0.262 mole) of furoyl chloride. Refluxing was maintained for four hours. The complex was decomposed with 60 ml. of sulfuric acid in ice, the organic layer separated and the aqueous extracted four times with 50-ml. portions of benzene. The organic layers were combined, washed thoroughly with 10% sodium carbonate solution and saturated sodium chloride solution, dried with calcium sulfate, filtered, and the solvent stripped, finally under reduced pressure. The residue was fractionated at 55–58° (3 mm.) to give 8 g. (27.7%) of 2-acetylfuran.

Furan-2-glyoxal. (a) From 2-Acetylfuran.—In a 1000-ml. 3-neck interjoint flask fitted with a sealed stirrer, reflux condenser and thermometer, was placed 39 g. (0.35 mole) of selenium dioxide, 220 ml. of dioxane and 7.5 ml. of water. The mixture was stirred at 50° until solution was complete. Thirty-eight grams (0.346 mole) of 2-acetylfuran was then added and the solution refluxed for four hours. The selenium was removed by filtration through a bed of Supercel and the solvent was removed from the filtrate by distillation through a short Vigreux column. Fractionation of the residue under a 30-cm. Vigreux column gave 20 g. (46.5%) of a yellow oil boiling at 65–66° (4 mm.).

b. From Furoyl Chloride.—2-Diazoacetylfuran and 2-chloroacetylfuran were prepared by the method of Burger.[2]

2-Furoylmethylpyridinium Chloride.—The chloroacetylfuran (9.4 g.) was mixed with 30 ml. of pyridine (dried over barium oxide), and warmed gently on the steam-bath. A vigorous reaction occurred, and a black tar was precipitated. Heating was maintained for one hour, at the end of which time the mixture was cooled and treated with anhydrous ether, leaving a gray powder which was recrystallized several times from *s*-butanol (Darco), giving 7.3 g. (50%) of white crystals melting at 178–179°.[13]

Anal.[14] Calcd. for $C_{11}H_{10}ClNO_2$: Cl, 15.85; N, 6.26. Found: Cl, 15.44; N, 6.31.

2-Furoyl-N-(4′-dimethylaminophenyl)-nitrone.—In a 500-ml. 3-neck flask fitted with a mechanical stirrer, thermometer, vent and dropping funnel was placed 7.3 g. (0.0326 mole) of the pyridinium chloride, 20 ml. of water and 5.35 g. (0.0356 mole) of *p*-nitrosodimethylaniline in 170 ml. of 95% ethanol. The solution was chilled to 0° and 36 ml. of 1 *N* sodium hydroxide was added during ten minutes, maintaining the temperature at 0 ± 3°. The mixture turned blood red in color and the odor of pyridine became apparent. Red crystals began to form within thirty minutes, and the crystallization was completed by the addition of cold water. The product was removed by filtration, washed thoroughly with water, air dried and recrystallized three times from a benzene–hexane mixture yielding 5.1 g. (61%) of deep red crystals melting at 123–125°.

Anal. Calcd. for $C_{14}H_{14}N_2O_3$: N, 10.85. Found: N, 11.21.

Furan-2-glyoxal Hydrate.—One and eight-tenths grams (0.007 mole) of the nitrone was mixed in a small separatory funnel with 20 ml. of 5 *N* sulfuric acid and 5 ml. of water. The green solution was extracted six times with 30 ml. of ether. The solvent layer was washed with a little saturated sodium bicarbonate solution, dried with calcium sulfate and the volatiles removed by distillation, leaving a colorless crystalline mass which could be recrystallized from a small quantity of benzene to give 0.7 g. (71%) of furan-2-glyoxal hydrate melting at 68–69°.

A sample of the hydrate prepared by treatment of anhydrous furan-2-glyoxal with two moles of water melted at 69–70° and gave no depression in melting point when admixed with that produced from the nitrone. In addition, both products gave similar green-blue colorations upon solution in acetic anhydride and treatment with a drop of concentrated sulfuric acid.

Furan-2-glyoxal Mono-semicarbazone.—Furanglyoxal was heated with one molecular equivalent of semicarbazide hydrochloride according to the directions of Shriner and Fuson.[15] The derivative was recrystallized three times from 2-ethylbutanol to a constant melting point of 215° (dec.).

Anal. Calcd. for $C_7H_3N_3O_3$: C, 46.71; H, 3.89. Found: C, 46.11; H, 3.95.

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(13) All melting points taken with a Fisher–Johns apparatus.

(14) Aanlyses by Oakwold Laboratories, Alexandria, Virginia.

(15) Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1946, p. 142.

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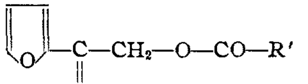
Acyloxyacetylfurans. II

BY HOWARD W. ALLCOCK,[1] FRANK KIPNIS,[1a] JOHN ORNFELT AND PAUL ALLEN, JR.

It has been reported by Kipnis and co-workers[2] that it is possible to prepare 2-acyloxyacetylfurans by the interaction of carboxylic acids with ω-diazoacetylfuran. The present work reports on the production of additional members of this series, synthesized by a variation of the original method. The diazoketone was transformed to 2-

TABLE I

ACYLOXYACETYLFURANS


R	R′	Yield, %	M. p.,[a] °C.	Empirical formula	Analyses,[b] % Calculated C	H	N	Found C	H	N
=O	-CH₃	59.5	31.5–32.5[c]	$C_8H_8O_4$	57.14	4.80		57.26	4.80	
=O	-(CH₂)₂CH₃	82.0	[d]	$C_{10}H_{12}O_4$	61.16	6.12		60.63	6.31	
=O	-C₆H₅	64.1	75.5–76	$C_{13}H_{10}O_4$	67.82	4.38		67.79	4.56	
=NNHCONH₂	-CH₃		95–95.5	$C_9H_{11}N_3O_4$			18.66			18.40
=NNHCONH₂	-(CH₂)₂CH₃		114–116	$C_{11}H_{15}N_3O_4$			16.59			16.46
=NNHCONH₂	-C₆H₅		180–182 dec.	$C_{14}H_{13}N_3O_4$			14.63			14.86
=NNHCONH₂	-C₄H₃O (furan)		122–123 dec.	$C_{12}H_{11}N_3O_5$			15.16			14.90

[a] Melting points taken with Fisher–Johns apparatus. [b] Carbon and hydrogen analyses by The Microlab, Staten Island, N. Y.; Kjeldahl nitrogen analyses by H. W. A. [c] B. p. 70–75° (0.1 mm.). [d] B. p. 110–112° (0.03 mm.).

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(1) Abstracted from a thesis submitted by H. W. A. to The Stevens Institute of Technology in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

(1a) Present address: Oxford Products, Inc., Cleveland, Ohio.

(2) Kipnis, Soloway and Ornfelt, THIS JOURNAL, **70**, 142 (1948).