The mixture was then brought to boiling and live steam passed through it until the total volume of distillate was 250 ml.

The steam distillate was extracted with two 75-ml. portions of ether and the ethereal extract dried over sodium sulfate. The ether was removed on the steam-bath and the residue vacuum-distilled: yield of phenylacetaldehyde, b. p. 87–88° (18 mm.), 5.4 g., 0.045 mole, 33%.

The other aldehydes studied were prepared by much the same procedure. The results are summarized in the table.

Aldehyde prepared	Time allowed for pptn. of addn. complex	Yield, %
Benzaldehyde[4]	5 hours	97
β-Naphthaldehyde[5]	12 hours	91
p-Tolualdehyde[4]	12 hours	77
Phenylacetaldehyde[4]	18 hours	33
Isocapraldehyde	7 days	31
o-Tolualdehyde[7,8]	8 days	9
α-Naphthaldehyde[7]	7 days	7
β-Hydroxypropionaldehyde[6]	7 days	0

(4) Reported by Stephen[2] in almost quantitative yields.

(5) One liter of hot water was added to the residue and live steam passed through the mixture as long as any solid came over in the steam distillate. The solid was recrystallized from 50% aqueous alcohol. Fulton and Robinson, *J. Chem. Soc.*, **152**, 200 (1939), reported the preparation of β-naphthaldehyde by the Stephen technique in 75% yield. Their work was published after the preparation had been completed at the University of Maryland.

(6) Removal of the aldehyde by steam distillation was not attempted; 500 ml. of water was added to the addition complex, the mixture warmed on the steam-bath for one hour, allowed to cool and extracted with ether. The product was a thick, tarry liquid which gave negative tests with Schiff and Tollens reagents.

(7) Reported by Stephen[2] in poor yield.

(8) There was no precipitate after seven days so one-half of the ether was removed and the reaction mixture allowed to stand another twenty-four hours.

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Crystalline Lead Orthophosphate

BY EDWARD J. ROEHL

In the preparation of crystalline metathetical reaction products where the solubility of the reaction product is very low, it is often difficult to obtain crystals large enough for microscopic examination, and a number of methods have been employed for maintaining the necessary slight supersaturation. The writer has successfully employed a cellophane membrane for a number of such cases.

By treating a solution of lead acetate with sodium hydrophosphate, Aiders and Stähler[1] succeeded in preparing lead orthophosphate, but without any signs of microscopically recognizable crystals. In fact, it appears from the literature that the only method of preparing this salt is the rather cumbersome one of Zambonini,[2] who fused

(1) Aiders and Stähler, *Ber.*, **42**, 2263 (1909).
(2) Zambonini, *Z. Kryst.*, **58**, 226 (1923).

and slowly cooled the white powder. In our experiments, a cellophane membrane was tied over the mouth of a test-tube (an open tube could of course be used) containing a 1% solution of Na_2HPO_4 and the tube inverted in a slightly acidified 0.2% solution of $Pb(C_2H_3O_2) \cdot 3H_2O$. At once an almost amorphous precipitate of lead orthophosphate appeared on the under side of the membrane and in about a minute crystals of the white salt started to fall.

The crystals (some of which were 2 mm. in length) were uniaxial hexagonal prisms exhibiting strong birefringence and showing an optically negative character. The values of $\omega = 1.970$ and $\epsilon = 1.936$ check the data in the literature for the refractive indices of lead orthophosphate. Analysis of the crystals gave a value of 17.4% as compared with the calculated value of 17.5% for $Pb_3(PO_4)_2$.
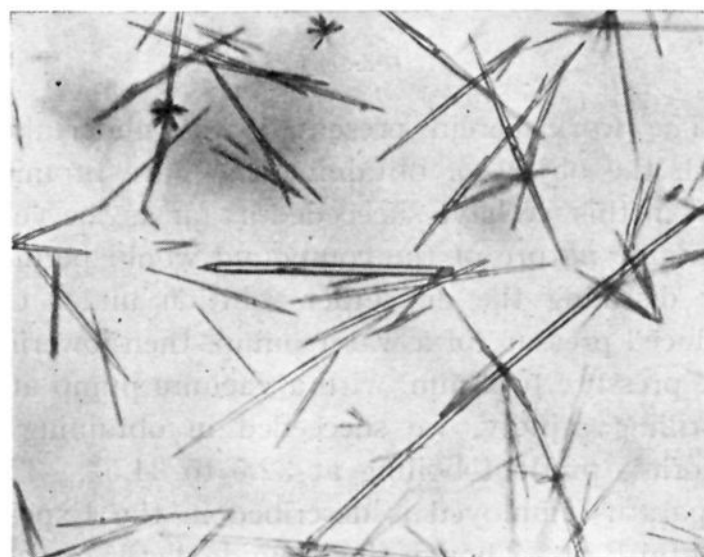

Fig. 1.

The accompanying photomicrograph at (50 ✕) shows some of the crystals obtained.

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α-Furfuryl Bromide (2-Bromomethylfuran)

BY J. E. ZANETTI AND J. T. BASHOUR

In 1927 one of us[1] prepared an ether solution of α-furfuryl bromide by acting on furfuryl alcohol with phosphorus tribromide. The solution proved satisfactory in the synthesis of various furfuryl ethers but the pure bromide was not separated as its decomposition was rapid once the solvent was evaporated. Von Braun and Kohler[2] had

(1) Zanetti, THIS JOURNAL, **49**, 1065 (1927).
(2) Von Braun and Kohler, *Ber.*, **51B**, 86 (1918).

had a similar experience when they synthesized the bromide by acting on α-furfurylmethylethyl-amine with cyanogen bromide in ether solutions; they were unable to obtain the pure compound from the ether solution. Recently the ether solution of the bromide has been used by Paul[3] in the synthesis of alkyl furans with the Grignard reagent and by Paul and Normant[4] in a study of the preparation of phenyl-α-furfuryl ether and its rearrangement.
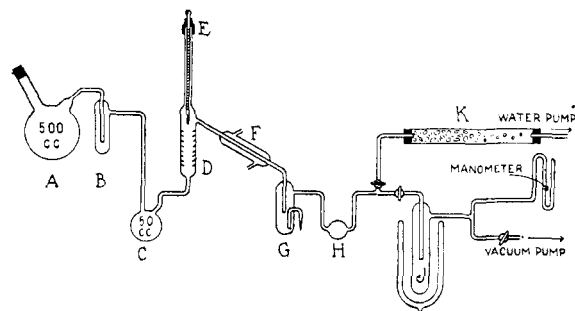

Fig. 1.

The work herein presented was undertaken with the object of obtaining the pure bromide and in this we have succeeded as far as the very unstable nature of the compound would permit. By distilling the dry ether solution under the reduced pressure of a water pump, then lowering the pressure to 2 mm. with a vacuum pump and distilling rapidly, we succeeded in obtaining a colorless product boiling at 32.5 to 34.5°. The apparatus employed is described in the Experimental Part. Though the bromide distils over as a colorless liquid, in a few minutes it begins to color yellow and then brown. Its rate of decomposition seems to be a function of the concentration of hydrobromic acid, which is one of the decomposition products. Hence it must never be kept long in a confined space as the rapidity of the decomposition reaches explosive violence. During a specific gravity determination a pycnometer containing 3 cc. of the bromide exploded a few minutes after being taken out of the balance case. The operator fortunately had moved far enough away so that he was not injured, but no trace of the pycnometer could be found except one of the caps closing the capillaries. Even when kept in loosely stoppered containers the decomposition is rapid the vessels becoming coated with tough graphitic films

(3) Paul, *Bull. soc. chim.*, [5] **2**, 2227 (1935).

(4) Paul and Normant, *ibid.*, [5] **5**, 1148 (1938).

similar to those described in the preparation of the α-furfuryl iodide.[5]

The bromide is slightly lachrymatory and a distinct lung irritant, the irritation not appearing for some hours after inhaling the vapor.

Density determinations gave d^{20}_{20} 1.560 and the index of refraction with the Abbe refractometer was n^{20} 1.5380. Chemically the compound was identified by condensing it with furfuryl alcohol to di-α-furfuryl ether, b. p. 100–102° at 2 mm.

Because of the short life and dangerous nature of this compound and the fact that the ether solution in which it is prepared is satisfactory for synthetic work, it did not appear of importance to carry this investigation any further.

Experimental

Preparation of the α-Furfuryl Bromide.—This was carried out as described by Zanetti[1] using smaller quantities (20 g. of furfuryl alcohol and 20 g. of phosphorus tribromide). The solutions stood from twenty to forty hours over granulated sodium hydroxide. The solutions were then rapidly filtered and distilled in the apparatus shown in Fig. 1.

Apparatus.—The apparatus consisted of a 500-cc. bulb (A) connected through a trap (B) with a smaller bulb (50 cc.) C. This was connected through a 5-cm. reflux column (D) with thermometer attachment (E) and a condenser (F) with another trap (G) provided with a siphon side-tube ending in a capillary. A small bulb (H) of 50-cc. capacity was inserted before trap (J) which was immersed in "dry-ice"–ethylene trichloride mixture and used to protect the vacuum pump. (K) was a drying tube to prevent water vapor from entering the apparatus. The entire apparatus was made of Pyrex glass. The only points where the compound might come in contact with organic material were at the side tube of (A) and at the thermometer holder (E) where a piece of rubber vacuum tube was used to hold the thermometer in place. The side-tube of (A) and the thermometer holder were made of 8-mm. tubing, the stoppered ends far removed from the warm vapors so that contamination from these sources was unappreciable.

Operation of the Apparatus.—The apparatus was first exhausted to 2 mm. and warmed to take out all moisture. Air was slowly let in through (J) till atmospheric pressure was reached. The filtered ether solution was then placed in (A) and the side-tube closed with a small cork thoroughly covered with collodion. The connection leading to the vacuum pump was closed and that leading to the water pump opened. When the water pump was started the boiling of the ether solution was rapid and the temperature dropped fast. In order to keep the ether boiling it was necessary to immerse (A) in water kept at about 30°. When no more ether came over, the vacuum pump was started and the pressure in the apparatus brought down to 2 mm. A small amount of ether col-

(5) Zanetti, THIS JOURNAL, **49**, 1061 (1927).

lected in (J). Ice water-baths were then placed around (B) and (C) and a hot water-bath around (A). Distillation of the bromide began accompanied by darkening and film formation in (A). The distillate collected mostly in (B). When distillation was finished, the bath around (B) was heated almost to boiling and an ice water-bath placed around (G). When this distillation was over, the bath around (C) was raised to boiling and an ice-bath placed under (H). This was the final distillation, the colorless bromide distilling into (G) while the temperature remained at 32.5 to 34.5°. A very small amount of distillate passed into the bulb (H). When the distillation was complete, the apparatus was brought back to atmospheric pressure by slowly letting air through (J). The side-tube capillary was then broken and the liquid siphoned off into a small flask by gently sucking out the air from the flask.

The residues in (A), (B) and (C) were black and tarry but the distillate in (G) was colorless throughout the distillation, though shortly after it began to color. Five runs were made, each with a new apparatus as it was found easier to discard the one used than to attempt to remove the graphitic films formed in it from the bromide decomposition.

The yields were about 50% of the theoretical.

Properties of the Compound.—As mentioned, the compound is a colorless liquid which decomposes rapidly, turning yellow then brown and ending in a tarry mass which adheres tightly to the container. Attempts to keep the compound for more than a few hours proved futile. Moisture doubtless plays an important role in initiating the decomposition. Phosphorus pentoxide or anhydrous sodium sulfate, however, proved useless in stabilizing the compound. Solid potassium hydroxide, though unable to prevent blackening, delays total decomposition for a much longer time. This points to the possibility that the hydrobromic acid formed by the decomposition may act as an accelerator. The compound thus prepared and dissolved in ether remains undecomposed for days.

Identification.—Analyses gave for bromine 50.3 and 49.0%, calculated, 49.66%.

Four and one-half grams of the bromide was condensed with excess of furfuryl alcohol and potassium hydroxide and the product distilled at 2 mm. The di-α-furfuryl ether came over at 100–102°; yield 85%.

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NEW YORK, N. Y.   RECEIVED MAY 5, 1939

COMMUNICATIONS TO THE EDITOR

HOMOGENEITY OF GONADOTROPIC HORMONE PREPARATIONS ISOLATED FROM PREGNANCY URINE

Sir:

We have reported the preparation from pregnancy urine of gonadotropic fractions containing 4000 minimal ovulating doses per milligram when assayed in the post-partum rabbit [*J. Biol. Chem.*, **128**, 525 (1939)]. Two such samples have recently been examined on the ultracentrifuge,[1] and appear to be homogeneous with respect to sedimentation. In each case, in the concentrations employed, a single sharply defined band was observed at approximately 250,000 times gravity.

In addition, electrochemical homogeneity of one of these preparations was demonstrated as a result of studies with the electrophoresis apparatus of Tiselius.[2] Evidence for the presence of only a single component (which previous analysis had shown to be a polypeptide-poly-

(1) Through the courtesy of Drs. A. E. Severinghaus and J. A. Chiles, Jr.

(2) Through the courtesy of Dr. Florence B. Seibert.

saccharide complex), was indicated by the appearance of a single migrating band having sharp boundaries in a phosphate buffer of ionic strength 0.1 (pH 7.0). The mobility was 4.85×10^{-5} cm.^{2}, sec.$^{-1}$, volt^{-1}.

Isoelectric point determinations, made by adsorbing the hormone upon collodion particles, and determining migration in a microelectrophoresis cell, showed an isoelectric point of pH 3.2–3.3.

Since such preparations appear to be identical with regard to biological activity and chemical composition, we feel that the evidence obtained with the ultracentrifuge and Tiselius apparatus demonstrates the homogeneity of our preparations.

Further detailed data bearing upon the physical and chemical properties of these and similar preparations of the hormone will be reported shortly.

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PHILADELPHIA, PA.   D. WRIGHT WILSON
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