jected to the action of ammonium polysulfide. From the cooled mixture obtained from 3-acetylpyrene, 1.95 g. (92%) of golden-brown centimeter-long prisms of practically pure **3-pyrenylacetamide** was filtered off and washed with a mixture of dioxane and ammonium polysulfide solution; m. p. 244–246°. A sample after sublimation at 240° and 0.01 mm. pressure crystallized from acetic acid–chlorobenzene in fine, colorless prismatic needles; m. p. 246–247°.

Anal.[11] Calcd. for $C_{18}H_{13}ON$: N, 5.41. Found: N, 5.39.

The unrecrystallized amide (13.7 g.) was dissolved in 200 cc. of boiling acetic acid, 100 cc. of concentrated hydrochloric acid was added cautiously through the top of the upright condenser attached to the flask, and the mixture was refluxed for one and one-quarter hours, when an additional 100 cc. of hydrochloric acid was added in order to precipitate the product. From the chilled mixture, the **3-pyrenylacetic acid** (13.4 g.; m. p. 218.5–220°) was filtered; it was purified through its water-soluble potassium salt and then recrystallized from chlorobenzene (130 cc.). The first crop of fine, slightly colored plates and prisms weighed 12.3 g. (90%); m. p. 222.5–223° (vac.) (reported,[6] 220°, dec.).

The same acid was obtained in poor yield by heating a mixture of 3-chloromethylpyrene (prepared from 3-pyrenylcarbinol and phosphorus trichloride) and potassium cyanide in methanol for one and one-half hours, followed by refluxing the nitrile with 20% alcoholic potassium hydroxide for twenty-two hours.

The amide (1.7 g.; m. p. 177–181°) obtained from 2 g. of 3-propionylpyrene was hydrolyzed in the manner described and the acid was purified through its salt. The **β-3-pyrenylpropionic acid** (1.42 g.; m. p. 173–174°) crystallized from acetic acid–chlorobenzene in pale tan platelets; m. p. 178–179°. It can be obtained colorless by sublimation at 0.01 mm. pressure. The same acid was obtained from 3-chloromethylpyrene through the malonic ester synthesis.

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.2; H, 5.1. Found: C, 83.1; H, 5.2.

The methyl ester was prepared by means of diazomethane; after evaporative distillation at 0.01 mm. pressure and recrystallization from methanol, it formed gleaming, colorless leaflets; m. p. 95.5–96.5°, cor. (reported,[12] 81°).

A 46% yield of **γ-3-pyrenylbutyric acid** was obtained as practically colorless crystals by hydrolysis of the 1.22 g. of crude amide (m. p. 172–175°) which was obtained from 2 g. of 3-*n*-butyrylpyrene; after recrystallization from a mixture of benzene, acetone and acetic acid, it melted at 186–187°, alone and when mixed with an authentic specimen.

Summary

The synthesis of the new 1′-methyl-3,4-benzpyrene from 3-acetylpyrene and new syntheses of 2′-methyl- and 3′-methyl-3,4-benzpyrene are described. 3′,4′-Dimethyl-3,4-benzpyrene also has been synthesized.

A study has been made of the Willgerodt reaction on five 3-acylpyrenes.

ANN ARBOR, MICHIGAN RECEIVED JULY 11, 1941

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[11] Micronalysis by Torsti Salo.

[CONTRIBUTION FROM AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

The System Trimethyl Phosphate–Water

BY H. ARMIN PAGEL AND FRANK S. MAXEY

The freezing points of trimethyl phosphate have been described in an earlier paper.[1] The accompanying data and graph show the freezing points of the system trimethyl phosphate–water, in which the solid phase of the ester is the so-called "alpha" form.

Experimental

The purified ester used in this work was the same as that used previously.[1] Likewise, the apparatus was the same except that reduced pressure was required to obtain sufficiently low temperatures with the solid carbon dioxide–alcohol mixture, when working near the ester–water eutectic composition. Weight burets were used to prepare the various ester–water mixtures to an accuracy within 0.1 mole per cent.

TABLE I

EXPERIMENTAL VALUES OF THE FREEZING POINTS OF THE SYSTEM TRIMETHYL PHOSPHATE–WATER

Mole % Me_3PO_4	F. p., °C.	Mole % Me_3PO_4	F. p., °C.
0.0	0.0	44.9	−64.0
2.2	− 2.1	47.0	−68.3
4.7	− 4.4	49.0	−72.0
6.8	− 6.3	50.0	−73.4
9.8	− 8.6	52.0	−77.0
13.5	−12.8	(Eutectic)	
19.4	−19.0	55.0	−72.8
21.0	−20.0	60.0	−67.0
24.5	−27.3	65.2	−62.4
27.5	−33.0	70.0	−58.7
32.5	−41.2	74.9	−55.4
35.0	−47.0	80.0	−52.8
36.4	−49.2	84.9	−50.2
39.0	−53.7	90.0	−49.1
40.0	−55.4	96.4	−47.1
41.0	−57.0	100.0	−46.1

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[1] Pagel and Schroeder, THIS JOURNAL, **62**, 1837 (1940).

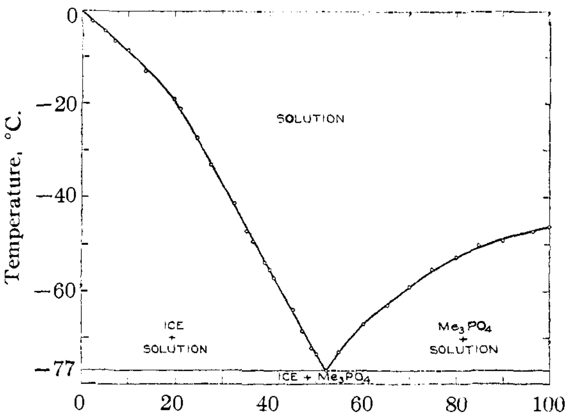

Fig. 1.—The system trimethyl phosphate–water.

Approximate freezing points of the various mixtures were first determined by supercooling several degrees below the anticipated freezing point and observing the maximum temperature rise obtained by seeding with a small amount of frozen solid of identical composition. After allowing the frozen fraction to melt, the mixture was again supercooled two-tenths to five-tenths of a degree below the approximate freezing point previously found, and seeded as before. The temperature gradient between the cooling bath and the ester–water mixture was controlled so that the change in freezing temperature due to the progressive freezing of the mixture was always less than 0.05° per minute. This allowed ample time to balance the potentiometer.

Discussion.—Mixtures ranging from about 35 to 80 mole per cent. of the ester were found to become decidedly viscous near their freezing points. Mixtures having compositions near that of the eutectic failed to freeze spontaneously even when cooled to −90°, and in such cases solid "seed" could be obtained only by seeding first with a small amount of the "alpha" solid ester.

The eutectic composition (52.0 mole % Me_3PO_4) was first estimated by extrapolation and then tested experimentally. The eutectic freezing point found was then checked by progressively freezing a 50.0 mole per cent. mixture which initially froze at −73.40° and fell to −77.00°, where the temperature remained constant until the mixture was practically frozen solid. This value agreed within 0.05° of that found for the extrapolated eutectic composition.

Summary

1. Freezing points of the system trimethyl phosphate–water have been studied.
2. The eutectic composition was found at 52.0 mole per cent. of the ester, with a freezing point of −77.0°.
3. Tabulated data, graphical representation and reference to experimental methods, and some discussion have been included.

LINCOLN, NEBRASKA RECEIVED JULY 7, 1941

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Dehydrogenation of Normal Heptane and Cyclohexane on Cerium, Vanadium and Thorium Oxide Catalysts*

BY RICHARD A. BRIGGS AND HUGH S. TAYLOR

In extension of our investigations on the dehydrocylization of normal heptane on chromium oxide catalysts, we have accumulated data on the aromatizing properties of the oxides of cerium, vanadium and thorium, published data being scanty and contained primarily in patents.[1,2,3,4] Moldavskii and Kamusher[5] investigated thorium oxide. In 1939, while this work was in progress, Koch[6] published data using narrow-boiling fractions of the product of the Fischer–Tropsch process, testing vanadium oxide.

Experimental Details

Apparatus.—The apparatus was essentially similar to that described in earlier work on chromium oxide catalysts.[7] In the final phase of the work the feed system for

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* Original manuscript received November 8, 1940.

[1] Wietzel and Pfaundler, U. S. Patent 1,910,910, May 1933; Convention Date, Nov. 1925.

[2] Mittasch, Pier, Wietzel and Langheinrich, U. S. Patents 1,913,940, 1,913,941, June 1933; Convention Date, Feb. 1926.

[3] Pier and Donath, U. S. Patent 1,975,476, Oct. 1934; Convention Date, Feb. 1926.

[4] Grosse and Morrell, U. S. Patents 2,124,566, 2,124,567, 2,124,583, 2,124,584, 2,124,585, 2,124,586.

[5] B. L. Moldavskii and H. D. Kamusher, *Compt. rend. Acad. Sci.* (USSR), **1**, 355 (1936).

[6] H. Koch, *Brennstoff-Chem.*, **20**, 1 (1939).

[7] S. Goldwasser and H. S. Taylor, THIS JOURNAL, **61**, 1260 (1939).