with activated charcoal, and reprecipitated with water. Recrystallization from aqueous ethanol gave 1.3 g. (72%) of 1,1-dichloro-2,2-bis-(*p*-*t*-butylphenyl)-ethylene (II), m. p. 137.6–138.6° (cor.).

Anal. Calcd. for $C_{22}H_{26}Cl_2$: Cl, 19.62. Found: Cl, 19.79.

To a refluxing solution of 199 mg. of the olefin II in 10 ml. of glacial acetic acid, 200 mg. of chromium trioxide was added portionwise. Refluxing was continued for one hour. The reaction mixture was cooled and poured onto ice; the resulting solid was washed by decantation with water, dilute sodium hydroxide solution, and water again. The solid was filtered, dried and recrystallized from methanol. The product, di-*p*-*t*-butylbenzophenone, crystallized as needles melting at 134.1–135.5° (cor.); the yield was 70 mg. (43%).

Anal. Calcd. for $C_{21}H_{26}O$: C, 85.66; H, 8.90. Found: C, 85.78; H, 9.02.

BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE
AGRICULTURAL RESEARCH ADMINISTRATION
U. S. DEPARTMENT OF AGRICULTURE STANLEY J. CRISTOL
BELTSVILLE, MARYLAND ROBERT A. HAYES
H. L. HALLER

RECEIVED MARCH 11, 1946

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p,p'-Dichlorobenzophenone Hydrazone

A mixture of 5.0 g. (0.02 mole) of *p,p'*-dichlorobenzophenone (m. p. 143–145°, Dow Chemical Company), 1.5 g. (0.025 mole) of 85% hydrazine hydrate (Eastman Kodak Company), and 45 ml. of dry isopropanol was heated in a sealed tube[1] at 150–160° for seven hours. The solvent was evaporated on the steam-bath and the residue crystallized from 1-1 carbon tetrachloride–petroleum ether (60–70°) to give 3 g. of small yellow crystals melting 91–93°; this is 56% of the theoretical yield. The compound did not form at reflux temperature, and the yield was only about 25% when absolute ethanol was used instead of isopropanol at 150–160°.

Anal. Calcd. for $C_{13}H_{10}Cl_2N_2$: Cl, 26.79. Found: Cl, 26.72.

This derivative was characterized by a Wolff-Kishner reduction to di-(*p*-chlorophenyl)-methane. A mixture of 2.23 g. (0.008 mole) of the hydrazone and sodium isopropylate prepared from 0.33 g. (0.014 atom) of sodium and 15 ml. of dry isopropanol was heated in a sealed tube at 160° for three hours. After evaporation of the solvent and crystallization of the residue from absolute ethanol, 0.4 g. (21%) of di-(*p*-chlorophenyl)-methane melting 54–55° was obtained. This product showed no depression in melting point when mixed with an authentic sample prepared according to Montagne.[2]

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(1) Grummitt and Hall, THIS JOURNAL, **66**, 1229 (1944).

(2) Montagne, *Rec. trav. chim.*, **25**, 379 (1906).

SHERWIN-WILLIAMS LABORATORY
WESTERN RESERVE UNIVERSITY OLIVER GRUMMITT
CLEVELAND, OHIO ALBERT JENKINS

RECEIVED MARCH 2, 1946

Tris-(hydroxymethyl)-phosphine Oxide Trilaurate

Tetra-(hydroxymethyl)-phosphonium chloride formed by the action of phosphine on a solution of hydrogen chloride and formaldehyde was converted to tris-(hydroxymethyl)-phosphine oxide by means of barium carbonate. Both reactions followed published procedures of Hoffman.[1] After removal of excess barium as sulfate, a concentrated aqueous solution of the oxide was subjected to a Schotten–Baumann reaction[2] with a slight excess of lauroyl chloride. The crude ester, obtained in 50% yield, was recrystallized from ether–petroleum ether and from methanol–benzene to give feathery crystals with a constant m. p. 65.5–66.5°.

Anal. Calcd. for $(C_{11}H_{23}COOCH_2)_3PO$: P, 4.51. Found (L. M. White): P, 4.36.

The crystallized product is soluble readily in benzene or chloroform, moderately in ether, and slightly in petroleum ether or methanol. It is insoluble in water.

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(1) A. Hoffman, THIS JOURNAL, **43**, 1684 (1921); *ibid.*, **52**, 2995 (1930).

(2) Shriner and Fuson, "Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., p. 47.

WESTERN REGIONAL RESEARCH LABORATORY
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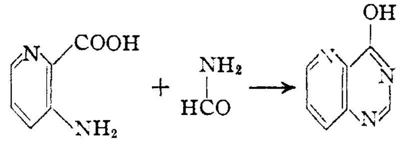
RECEIVED MARCH 5, 1946

4-Hydroxypyrido[3,2-*d*]pyrimidine[1]



β-Amino-*α*-picolinic acid was prepared from quinolinic acid essentially according to the directions of Sucharda.[2] A 13-g. sample was heated with 8 g. of formamide at 120–130° for two and one-half hours, at 160° for one-half hour and at 170–180° for two hours. The crystalline solid formed (4.3 g., 31%) was collected and washed with water. It separated from aqueous alcohol as white crystals, m. p. 346–347°.

Anal. Calcd. for $C_7H_5N_3O$: C, 57.15; H, 3.43; N, 28.56. Found: C, 57.12; H, 3.54; N, 28.64.

A number of attempts to replace the hydroxyl group with a chlorine atom by the usual procedures failed.

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(1) The work reported here was carried out under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and the University of Illinois.

(2) Sucharda, *Ber.*, **58**, 1727 (1925).

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS CHARLES C. PRICE
URBANA, ILLINOIS DAVID Y. CURTIN

RECEIVED FEBRUARY 4, 1946

6-Methoxy-8-(9-diethylaminononylamino)-quinoline Dihydrobromide[1]

Nonamethylene chlorohydrin, b. p. 100–110° (2 mm.), m. p. 26° (lit.,[2] 28°), was prepared in 60% yield essentially according to the directions of Bennett and Mosses.[2] Treatment with diethylamine under pressure at 140° produced the aminoalcohol in 80% yield, b. p. 130–132° (3 mm.), n^{20}D 1.4572 (lit.,[3] b. p. 161.5° (12 mm.), n^{19}D 1.4574). This was converted to the bromide hydrobromide by boiling 42% hydrobromic acid followed by removal of the excess hydrobromic acid by evaporation under diminished pressure at 95°. The salt was then condensed with 6-methoxy-8-aminoquinoline by boiling in a small amount of absolute ethanol. The product, obtained in 53% yield from the aminoalcohol,[4] boiled at 210–214° (0.5 mm.), n^{20}D 1.5562 (lit.,[3] b. p. 218° (0.5 mm.), $n^{17.2}$D

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(1) The work reported here was carried out under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and the University of Illinois.

(2) Bennett and Mosses, *J. Chem. Soc.*, 1697 (1931).

(3) Altman, *Rec. trav. chim.*, **57**, 941 (1938).

(4) Altman (ref. 3) converted the aminoalcohol to the aminoalkyl chloride with thionyl chloride. The subsequent condensation was then carried out in a sealed tube at 130 to 170°; no yield was reported.

1.5569). The alkylated aminoquinoline was very susceptible to air-oxidation, and it was necessary to preserve it under nitrogen in the cold.

Anal. Calcd. for $C_{23}H_{37}N_3O$: C, 74.34; H, 10.04. Found: C, 74.50; H, 10.14.

Attempts to prepare the dihydrochloride were unsuccessful, but it was found that the **dihydrobromide** could be prepared easily. To 10 g. of the free amine was added a solution of 10 ml. of 40% hydrobromic acid (sp. g. 1.38) in 100 ml. of absolute ethanol and 100 ml. of absolute ether. The salt separated as a fine, yellow powder, m. p. 192.5–193.5°, when the solution was cooled. The analytical sample was crystallized from hot absolute ethanol.

Anal. Calcd. for $C_{23}H_{39}Br_2N_3O$: C, 51.79; H, 7.34; Br, 29.97. Found: C, 51.71; H, 7.11; Br, 29.97.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
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CHARLES C. PRICE
HARRY F. HERBRANDSON

RECEIVED FEBRUARY 4, 1946

COMMUNICATIONS TO THE EDITOR

FRACTIONATION OF CELLULOSE

Sir:

In the course of our work on the fractionation of cellulose by a refined procedure using cuprammonium solvent at low temperatures (below 0°), we have observed phenomena similar to those recently reported by Morey and Tamblyn[1] for cellulose acetate and cellulose acetate butyrate which demonstrate the importance of the choice of solvent and precipitant in fractionation work.

With cellulose the choice of solvent is limited, but with cuprammonium, which is recognized as the best solvent, we have found the choice of precipitant to be important.

For example, when a 5% aqueous solution of sodium potassium tartrate (Rochelle salt) was used as the precipitant, precipitation of fractions took place on a weight basis, but the respective fractions did not show a significant amount of resolution on a molecular weight basis. However, by selecting other precipitants, varying degrees of resolution on a molecular weight basis became possible, as illustrated in Table I.

TABLE I

FRACTIONATION OF CELLULOSE

Experimental rayon tire yarn; 100% wood pulp base; av. basic D. P. = 490.

	Sodium potassium tartrate soln.		Acetone		*n*-Propyl alcohol	
Fraction	% Recov.	Basic D. P.	% Recov.	Basic D. P.	% Recov.	Basic D. P.
1	19.7	480	46.6	535	18.8	615
2	19.3	478	13.2	392	20.2	465
3	18.3	473	8.5	314	20.8	316
4	17.5	470	18.4	250	16.6	272
5	13.4	470	8.1	142	9.7	247
6	13.7	478	..	...	6.1	132

The average molecular chain length values of the fractions are expressed as Basic D. P.'s.[2]

The same general phenomena have been observed for the fractionation of viscose rayons, and viscose rayon pulps, respectively, from cuprammonium solvent.

Further work is in progress in which additional precipitants possessing wide variations in molecular structure are being used with the hope that resolving power can be correlated with molecular structure.

CHEMICAL RESEARCH DEPARTMENT
AMERICAN VISCOSE CORPORATION
MARCUS HOOK, PENNSYLVANIA
O. A. BATTISTA
WAYNE A. SISSON

RECEIVED APRIL 20, 1946

A REACTION VELOCITY WITH LARGE NEGATIVE TEMPERATURE COEFFICIENT

Sir:

Iodine shows very large departures from Raoult's law in a number of solvents, and it occurred to me to use iodine solutions to decide between activity and concentration as the determinant for reaction velocity. I chose the reaction between iodine and chlorine to form ICl, in CCl_4 to begin with, as one likely to meet the specifications. As so often happens in scientific research, it is not answering the original question, but has yielded results of such interest as to seem worth this brief preliminary report. They are as follows:

(1) The reaction is accelerated by light, but this is neither surprising nor disturbing, since one can let it proceed in the dark.

(2) It is enormously sensitive to minute traces of water. Although the solubility of water in CCl_4 is extremely small, the reaction runs to completion in minutes if the solutions are not carefully dried, whereas hours are required if the solutions are mixed after being kept sealed for a day in contact with P_2O_5.

(3) The "wet" reaction appears to be bimolecular, but the "dry" reaction is monomolecular with respect to chlorine through a wide range of iodine concentrations.

(4) And this is the truly astonishing feature, the wet reaction not only proceeds several times

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[1] D. R. Morey and J. W. Tamblyn, *J. Phys. Chem.*, **50**, 12–22 (1946).

[2] O. A. Battista, *Ind. Eng. Chem., Anal. Ed.*, **16**, 351–354 (1944).