of the addition product with acetic acid, as described in the reference quoted, produced emulsions. Decomposition with dilute sulfuric acid[5] was entirely satisfactory.

Diethyl β-Methylmalate.—Using a proportion of 1 g. of platinum oxide catalyst per mole of ethyl ethoxalylpropionate and an initial hydrogen pressure of from 3 to 4 atmospheres, the reduction of from 0.1 to 0.5 mole of the ester was complete within from two to three hours, as shown by the cessation of the uptake of hydrogen and a negative color test with ferric chloride. The use of a greater proportion of catalyst accelerated the reaction but resulted in heating of the reaction mixture. The use of a solvent (ethanol redistilled from sodium hydroxide) was disadvantageous: in several runs, the reaction slowed sharply when two-thirds complete and reached completion only after many hours; addition of fresh catalyst was ineffective.

In six runs, yields of from 88 to 92% were obtained of material boiling at 121-124° (10 mm.) and having $n^{25}\text{D}$ 1.4332-1.4338. Extrapolation from the data of Wislicenus[3a] indicated a b. p. of 125° (10 mm.); Wojcik and Adkins[3e] gave 109-113° (5 mm.); Abbot and McKenzie[3b] gave 116° (11.5 mm.).

β-Methylmalic Acid.—In a typical experiment, a mixture of 20.4 g. (0.10 mole) of diethyl β-methylmalate, 80 ml. of water and 1 ml. of 12 *N* hydrochloric acid was boiled under reflux and the course of the hydrolysis was followed by titrating samples against 0.05 *N* sodium hydroxide. There was no increase in acidity after five hours. The contents of the flask were reduced *in vacuo* to a sirup, and dehydrated by placing the flask in a vacuum desiccator containing sodium hydroxide and connected to a vacuum pump (Hyvac). After twenty-four hours, the product formed a very viscous colorless sirup weighing 15.16 g., compared with a theoretical recovery of 14.50 g.

Thymine.—Six grams (0.10 mole) of urea was added in small increments to 25 ml. of fuming sulfuric acid (15% SO_3) cooled in a bath of ice and salt. The mixture was brought to room temperature, stirred until all of the urea dissolved, and poured onto 7.4 g. (0.05 mole) of β-methylmalic acid prepared in the manner described above. After the latter had dissolved, the mixture was heated on a steam-bath for an hour. The reaction mixture was cooled, poured into 75 ml. of water and cooled to 0°. The product was filtered off, washed with water and recrystallized from the minimal volume of water (120 ml.) that would dissolve it at the boiling point. Yield, dried over phosphorus pentoxide *in vacuo*, was 3.15 g., or 50%, based on the amount of diethyl β-methylmalate taken at the start; m. p. 313-314° (uncor.) with decomposition.

Anal. Calcd. for $C_5H_6O_2N_2$: N, 22.23. Found: N, preparation 1, 22.28; preparation 2, 22.16 (micro-Kjeldahl; each value is the mean of four determinations).

Synthesis Directly from Diethyl β-Methylmalate.—The foregoing procedure was modified by substituting for β-methylmalic acid an equimolar amount of diethyl β-methylmalate, which was added to the solution of urea in sulfuric acid with stirring and cooling. The yield was 39%. In a second experiment, the amount of sulfuric acid was increased by one-third and the yield was 42%. Evidently, the concentration of acid was not critical.

Microbiological Assay.—Through the courtesy of Dr. I. C. Gunsalus of Cornell University, one of the present preparations of thymine was tested for its activity as a stimulant of the growth of *Streptococcus faecalis* R[6] and was found to be as effective as a sample of thymine prepared in another laboratory by the method of Johnson.[7]

5-Methylisocytosine.—Nineteen and one-tenth grams (0.20 mole) of guanidine hydrochloride was added in small increments to 54 ml. of fuming sulfuric acid (15% SO_3) cooled in a bath of ice and salt. The solution was brought to room temperature and poured onto 14.8 g. (0.10 mole) of β-methylmalic acid prepared in the manner already described. After the latter had dissolved, the solution was heated on a steam-bath for an hour, cooled, and poured into 2 liters of ice and water. Barium carbonate was added until, after stirring for half an hour, the solution was alkaline to congo red; a total of 300-325 g. of barium carbonate was required. The barium sulfate was filtered off and washed on the filter with 500 ml. of water. The filtrate was acidified with 0.2 ml. of concentrated sulfuric acid (to remove excess barium) and hydrochloric acid until acid to congo red (to hold the product in solution during subsequent concentration). The solution was reduced *in vacuo* to less than 100 ml., freed of barium sulfate by filtration, and neutralized to phenol red with concentrated ammonium hydroxide. After several hours of refrigeration, the product was filtered off and washed on the filter with 30-40 ml. of water. It recrystallized in rosets of needles from the minimal volume of water (325 ml.) that would dissolve it at the boiling point. The yield, dried over phosphorus pentoxide *in vacuo*, was 9.49 g., or 76%, based on the diethyl β-methylmalate taken at the start; m. p. 290-291° (uncor.), with slight carbonization and considerable evolution of gas.

Anal. Calcd. for $C_5H_7ON_3$: N, 33.60. Found: N, 33.67 (micro-Kjeldahl, mean of four determinations).

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[5] Wislicenus and Arnold, *Ann.*, **246**, 329 (1888).

[6] Stokes, *J. Bact.*, **48**, 201 (1944).

[7] Johnson, *J. Biol. Chem.*, **3**, 299 (1907).

NEW COMPOUNDS

1-Trichloro-2,2-bis-(*p*-*t*-butylphenyl)-ethane and Degradation Products[1]

To a mixture, kept at 30°, of 13.4 g. (0.1 mole) of *t*-butyl benzene and 7.4 g. (0.05 mole) of chloral was added dropwise, with stirring, 30 ml. of 100% sulfuric acid, after which the stirring was continued for one hour. The resulting mixture was poured upon ice and the solid washed by decantation, first with water, then with sodium bicarbonate, and finally with water again. The air-dried material weighed 14.5 g. and melted at 120-139°. After several recrystallizations from 95% ethanol, the product, 1-trichloro-2,2-bis-(*p*-*t*-butylphenyl)-ethane (I), melted at 154-155° (cor.) and was obtained in 33% yield.

Anal. Calcd. for $C_{22}H_{27}Cl_3$: Cl, 26.74. Found: Cl, 26.61.

The *para* position of the *t*-butyl groups is assumed on the basis of experience in the Baeyer condensation,[2] as well as upon the correspondence between the observed and predicted reaction-rate constants for dehydrochlorination with ethanolic sodium hydroxide as reported previously.[3]

A solution of 2.0 g. (0.005 mole) of I and 1.0 g. (0.018 mole) of potassium hydroxide in 30 ml. of 95% ethanol was heated at reflux for one and one-half hours. The reaction mixture was cooled, poured into water, and extracted with ether. The solvent was removed in an air stream, and the residue was taken up in ethanol, clarified

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[1] Part of a program supported by a transfer of funds, as recommended by the Committee on Medical Research, from the Office of Scientific Research and Development to the Bureau of Entomology and Plant Quarantine.

[2] (a) v. Baeyer, *Ber.*, **5**, 25, 280, 1094 (1872); (b) Fischer, *ibid.*, **7**, 1190 (1874); (c) Elbs, *J. prakt. Chem.*, [2] **47**, 68 (1893); (d) Grummitt, Buck and Stearns, THIS JOURNAL, **67**, 156 (1945); (e) Haller, Bartlett, Drake, Newman and co-workers, *ibid.*, **67**, 1591 (1945).

[3] Cristol, *ibid.*, **67**, 1494 (1945).

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
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BELTSVILLE, MARYLAND ROBERT A. HAYES
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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
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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.

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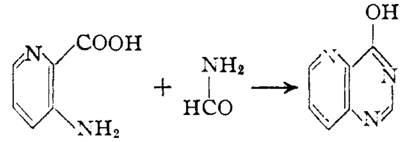
RECEIVED MARCH 5, 1946

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).

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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.