Preparation of 1,2-Dialkylcyclohexanes.—Preliminary tests showed that the 1,2-dialkylcyclohexenes were resistant to hydrogenation at room temperature and 1–2 atmospheres of hydrogen using platinum as catalyst. Hydrogenation occurred smoothly in a bomb at 150° and a starting hydrogen pressure of 2400 p. s. i. using 0.5–1.0 g. of Raney nickel catalyst for 2–5 g. of cyclohexene. Absolute ethanol (30–50 ml.) was used as solvent in all cases. After filtration the solution was evaporated to approximately 10 ml. and poured into water. The mixture was extracted with benzene and the combined extracts dried over sodium sulfate. After evaporation of the solvent the residue was treated with concentrated sulfuric acid to remove any cyclohexenes. The mixture was diluted with water and was extracted with benzene which was washed with dilute sodium hydroxide and water and dried over sodium sulfate. On distillation colorless liquids were obtained. Data on the cyclohexenes prepared are given in Table III.

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RECEIVED JUNE 21, 1949

Preparation of 2-Pyridylmethanol[1]

BY WALTER M. EDWARDS[2] AND PEYTON C. TEAGUE[3]

Harries and Lenart[4] and Graf, *et al.*,[5] have reported the preparation of 2-pyridylmethanol by methods which require several steps beginning with readily obtainable derivatives of pyridine. This report describes a simple method of preparation of 2-pyridylmethanol from 2-picoline, which does not involve the isolation of any intermediate product. 2-Picolyllithium was prepared by the hydrogen–metal interchange reaction between 2-picoline and phenyllithium. The picolyllithium was oxidized with a slow current of air to form the desired 2-pyridylmethanol.

A compound, $C_{12}H_{12}N_2$, was obtained as a by-product of the reaction. This compound was not identified but is probably 1,2-dipyridylethane, which would be expected[6] as the coupling product of two pyridyl radicals.

Experimental[7]

2-Picolyllithium was prepared by the procedure of Finkelstein and Elderfield[8] from 46.5 g. of 2-picoline. When the reaction was complete, the source of nitrogen was removed. Dry, carbon dioxide-free air was drawn at the rate of 2 cc. per minute into the flask and over the surface of the solution. The oxidation was carried out with stirring and without heating or cooling for eight hours, at which time the bright red color had disappeared and the mixture was light yellow. From time to time, more anhydrous ether was added to replace that lost by evaporation.

For the separation of the product, 6 *N* hydrochloric acid was added until the solution was acid to congo red. The aqueous layer was separated, made alkaline with sodium carbonate, saturated with sodium chloride, and extracted several times with chloroform. After the chloroform layer had been dried over anhydrous calcium sulfate for twenty-four hours, the chloroform and 2-picoline was distilled from the mixture at atmospheric pressure. The picoline boiled at 128° and was identified by the melting point of its picrate (168°). It weighed 11.3 g. or 24% of the original amount added.

The mixture of free bases was then fractionally distilled under reduced pressure. The following fractions were obtained: Fract. 1 (70–103° at 3–4 mm.), 11.2 g.; fract. 2 (103–136° at 3–4 mm.), 8.0 g., fract. 3 (138–170° at 1–2 mm.), 0.9 g.; residue, 16 g.

Identification of 2-Pyridylmethanol.—Fraction 1 on redistillation boiled completely at 111–115° at 16 mm. *Anal.* Calcd. for C_6H_7NO: N, 12.84. Found: N, 12.64. The picrate melted at 150° and the chloroplatinate at 179°. These data are in agreement with the values of Harries and Lenart.[4]

The yield of 11.2 g. was 20.5% based on the 2-picoline added or 27.0% on the basis of 2-picoline consumed in the reaction.

Compound $C_{12}H_{12}N_2$.—Fraction 2 redistilled at 112–114° at 1–2 mm. The distillate solidified on standing. After recrystallization from ligroin, its melting point was 49°. *Anal.* Calcd. for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21. Found: C, 77.98; H, 6.67; N, 15.05. Molecular weight determination by the Rast camphor method. Calcd.: 184. Found: 197, 196, 193; av. 195. This product was not further characterized.

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RECEIVED APRIL 27, 1949

(1) Abstracted from the thesis of Walter M. Edwards, submitted in partial fulfilment of the requirements for the M.S. degree at the University of Georgia, Athens, Georgia.

(2) Present address: Ohio State College, Columbus, Ohio.

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(4) Harries and Lenart, *Ann.*, **410**, 107 (1915).

(5) Graf, *et al.*, *J. prakt. Chem.*, **146**, 88 (1936).

(6) Gilman and Pacevitz, THIS JOURNAL, **61**, 1603 (1939).

(7) All melting points and boiling points are corrected.

(8) Finkelstein and Elderfield, *J. Org. Chem.*, **4**, 365 (1939).

Polyvinyl Bromide[1]

BY DAVID EDELSON AND RAYMOND M. FUOSS

In connection with our work on polyelectrolytes,[2] we attempted to prepare a polymeric quaternary compound by the addition of tertiary amines to polyvinyl bromide. The desired product was not obtained, but the results of some of our experiments seem worth reporting. Vinyl bromide is one of the earliest known vinyl compounds; Regnault[3] prepared it by treating ethylene dibromide with alkali. Staudinger[4] studied its polymerization and noted that the polymer readily loses hydrogen bromide.

We heated 0.5 cc. of 30% hydrogen peroxide and 10 g. of vinyl bromide[4a] in a bomb at 47° for twenty-four hours and obtained no polymer, although Güyer and Schütze[5] report complete conversion in twenty hours at 60°. About 30% conversion was obtained in two days at 60° from a (deoxygenated) solution of vinyl bromide (10 g.) in toluene (8 g.) saturated with benzoyl peroxide. The product was white, but darkened on drying under vacuum at 30°; Parr bomb bromine averaged to 70.2% (theoretical 74.77%). Fair results were obtained by photochemical

(1) Project NR 054-002 of the Office of Naval Research.

(2) R. M. Fuoss and G. I. Cathers, *J. Polymer Sci.*, **2**, 12 (1947); **4**, 97 (1949); R. M. Fuoss and U. P. Strauss, *ibid.*, **3**, 246 (1948); G. I. Cathers and R. M. Fuoss, *ibid.*, **4**, 121 (1949).

(3) V. Regnault, *Ann. chim.*, [II] **59**, 358 (1935).

(4) H. Staudinger, M. Brunner and W. Feisst, *Helv. Chim. Acta* **13**, 805 (1930).

(4a) We are indebted to the Dow Chemical Company for the sample of vinyl bromide on which these experiments were made.

(5) A. Güyer and H. Schütze, *Helv. Chim. Acta*, **17**, 1544 (1934).

polymerization[6] in ether solution in a sealed quartz tube placed in front of a 100-watt quartz mercury arc, but the product darkened in the tube unless precautions were taken to shield the polymer from the ultraviolet radiation.

Oxidation-reduction polymerization[7] using the recipe: 75 cc. of deoxygenated water, 2 g. of Cetab, 10 cc. of 1.0 *N* sulfuric acid, 13 g. of vinyl bromide, 1 cc. of 0.01 *N* ferrous sulfate in *N*/10 sulfuric acid and 1 cc. of 0.01 *N* hydrogen peroxide gave no yield, possibly as a consequence of the difficulty of deoxygenating a monomer which boils at 15.8°. Some conversion was obtained with potassium persulfate as catalyst, using the procedure described by Kolthoff and Dale.[8]

The polyvinyl bromide obtained by solution polymerization was insoluble in Bu_3N (cohesive energy density 44), petroleum ether (52), carbon tetrachloride (73), nitromethane (143), ethyl alcohol (260), and methyl alcohol (346); swelled in toluene (75), benzene (81) and acetone (91); and dissolved in methyl ethyl ketone (80), dioxane (91), $C_6H_5NO_2$ (102) and C_5H_5N (105). From these data, we estimate that the cohesive energy density[9] of polyvinyl bromide is about 90, approximately the same as that of polyvinyl chloride.[10]

Addition of polyvinyl bromide to pyridine in a conductance cell at 25° produced electrolyte, as shown by a rapid increase in conductance. Reaction with triethylamine and with trimethyl amine in methanol also lead to electrolyte formation. No polyelectrolyte was produced, however; in every case, an insoluble red-to-dark-brown precipitate was obtained, and tertiary amine hydrobromide was found in the supernatant liquid. This result shows that tertiary amines dehydrohalogenate polyvinyl bromide[11] in preference to adding to it to form a polymeric quaternary salt. Two facts favor the elimination of hydrogen bromide: first, steric hindrance militates against the insertion of an R_3N group at every other carbon of the polymer chain; and, second, any single elimination of hydrobromic acid produces labile allylic bromines (—CHBr·CH=CH—) in the chain, which are more reactive than the original bromine atoms of the polymer. The tendency thus is to produce conjugated segments in the polymer chain. If the elimination of hydrogen bromide is purely statistical,[12] occasional methylene groups will be isolated, which will break the conjugation. From the deep color and the insolubility of the product, however, we conclude that the conjugated segments must be quite long, in analogy to the higher members[13] of the $R(CH{=}CH)_nR'$ series.

(6) C. S. Marvel and E. H. Riddle, THIS JOURNAL, **62**, 2666 (1940).

(7) J. H. Baxendale, M. G. Evans and J. K. Killiam, *J. Polymer Sci.*, **1**, 466 (1946); A. G. Evans and E. Tyrrall, *ibid.*, **2**, 387 (1947).

(8) I. M. Kolthoff and W. J. Dale, THIS JOURNAL, **67**, 1672 (1945).

(9) J. H. Hildebrand, "Solubility of Non-Electrolytes," A. C. S. Monograph 17, Reinhold Publishing Corp., New York, N. Y., 1936.

(10) P. M. Doty and B. H. Zimm, Bulletin of the High Polymer Clinic, Polytechnic Institute of Brookyn, N. Y., 1946.

(11) C. R. Noller and R. Dinsmore, THIS JOURNAL, **54**, 1025 (1932).

(12) R. F. Boyer, *J. Phys. Colloid Chem.*, **51**, 80 (1947).

(13) R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, **11**, 87 (1928); G. Compton and W. Bergmann, *J. Org. Chem.*, **13**, 363 (1947).

STERLING CHEMISTRY LABORATORY
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Inhibition of Growth of *Escherichia coli* by 4-Aminopteroylglutamic Acid and its Reversal

BY A. L. FRANKLIN, E. L. R. STOKSTAD, C. E. HOFFMANN, M. BELT AND T. H. JUKES

Recent investigations[1-5] have shown that thymidine and certain other desoxyribosides can replace vitamin B_{12} as a growth factor for various lactic acid bacteria. In the present study, the relation of these desoxyribosides to the reversal of the inhibitory effect of 4-aminopteroylglutamic acid[6] (4-amino PGA), a potent antagonist of PGA, was measured. It was found that the growth of *Escherichia coli* was inhibited by high levels of 4-amino PGA in spite of the fact that the organism does not need PGA for growth. The inhibition was found to be reversed by liver extract or thymidine but not by PGA, *p*-aminobenzoic acid, vitamin B_{12}, thymine, guanine, hypoxanthine, adenosine, adenylic acid, cytidylic acid or the desoxyribosides of guanidine and hypoxanthine (Table I).

It was also found that *Lactobacillus leichmannii* 313, which needs both PGA (or *p*-aminobenzoic acid) and vitamin B_{12} for growth, was inhibited by 4-amino PGA. This inhibition was reversible by PGA at low levels of 4-amino PGA, up to 5 γ per ml., but at high levels of 4-amino PGA, 25 γ per ml., PGA was ineffective while thymidine produced a reversal. The desoxyribosides of guanine and hypoxanthine were ineffective as reversing agents, although these two compounds produced approximately maximum growth in the presence of PGA if 4-amino PGA and B_{12} were omitted. In the absence of 4-amino PGA, thymidine produced an incomplete growth response, about 50% of maximum, if PGA and *p*-aminobenzoic acid were omitted, with or without the addition of vitamin B_{12}. The response to guanine desoxyriboside or hypoxanthine desoxyriboside under these conditions was 25 to 33% of maximum.

Experimental

The liver extract was a commercial antipernicious-anemia preparation, 10 units per ml. The medium used

(1) Shive, Ravel and Eakin, THIS JOURNAL, **70**, 2614 (1948).

(2) Snell, Kitay and McNutt, *J. Biol. Chem.*, **175**, 473 (1948).

(3) Hoffmann, Stokstad, Franklin and Jukes, *ibid.*, **176**, 1467 (1948).

(4) Kitay, McNutt and Snell, *ibid.*, **177**, 993 (1949).

(5) Hoff-Jorgensen, *ibid.*, **178**, 525 (1949).

(6) Seeger, Smith and Hultquist, THIS JOURNAL, **69**, 2567 (1947).