peaks due to the parent molecules were left, *i.e.*, until the CH_3^+ peak from CH_4 had been eliminated.

The results obtained using this method of analysis on a mixture of CH_4 and CD_4 are given in Table I. Table II shows a typical set of results obtained for the analysis of a mixture containing four of the methanes. The precision with which the values could be measured has been indicated.

TABLE I

ANALYSIS OF CH_4–CD_4 MIXTURE

Compound	Analysis at low electron voltage, %	Calculated composition, %
CH_4	66.8 ± 0.4	61.2
CHD_3	1.8 ± .2	1.9
CD_4	31.4 ± .5	36.9

TABLE II

ANALYSIS OF DEUTERATED METHANE MIXTURE

Compound	Analysis at low electron voltage, %	Calculated composition, %
CH_4	35.8 ± 0.6	33.3
CH_3D	33.9 ± .4	32.0
CHD_3	1.5 ± .2	1.6
CD_4	28.8 ± .4	33.0

It can be seen from the results given above that the method of Stevenson and Wagner gives rise to serious errors if used as a general method of analysis for mixtures of deuterated methanes. This is apparently due to the relatively large differences between the ionization potentials of the methanes, as determined by electron impact. For the worst case, that of mixtures containing both CH_4 and CD_4, the CD_4 estimation can be in error by about 15%. It appears likely that a mixture of any successive pair of methanes (CD_nH_{4-n}–$CD_{n+1}H_{3-n}$) can be analyzed by this method with about the same accuracy as a mixture of CH_4 and CH_3D. For methanes farther apart in the series the error increases rapidly.

Very little information is available concerning the effect of deuteration on the ionization potentials of higher hydrocarbons. However, it has been shown[2] that for both acetylene and ethylene the ionization potential of the undeuterated compound is the same as that of the completely deuterated compound within 0.02 e.v. Thus, it would seem that the method of Stevenson and Wagner could be used to analyze, with good accuracy, mixtures of deuterated higher hydrocarbons. The method would be restricted to those cases where the appearance potential of interfering fragments is a volt or two greater than that of the parent molecule.

NATIONAL RESEARCH LABORATORIES
OTTAWA, CANADA

RECEIVED JULY 16, 1951

NEW COMPOUNDS

1,6-Dibenzyl-3,4-isopropylidene-D-mannitol

A sodium benzyloxide solution was prepared according to the directions of Tishler[1] from 5.5 g. of freshly cut sodium, rinsed with petroleum ether, and 110 ml. of dry (by distillation) benzyl alcohol. Three grams of 1,2;5,6-dianhydro-3,4-isopropylidene-D-mannitol[2] was added and dissolved, and the solution was heated with steam in a jacketed flask under reflux for 24 hours. The reaction mixture was then diluted with chloroform at 0° under vigorous stirring, the sodium benzyloxide was decomposed with cracked ice, and the organic layer which separated was dried over sodium sulfate. After removal of the chloroform at the water-pump, the benzyl alcohol solution was fractionated under high vacuum. The fraction collected at 0.02 mm. and a bath temperature of 160–190° was shown by acetone analysis to contain the desired product, and on redistillation at 0.02 mm. 1,6-dibenzyl-3,4-isopropylidene-D-mannitol came over at 195° (bath temperature). The product was a yellowish, viscous sirup having $n^{25}D$ 1.5395 and $[\alpha]^{23}D$ +10.8° (*c*, 5.2 in chloroform). An 0.25-mmole sample dissolved in glacial acetic acid absorbed 2.04 mmoles of hydrogen in 2.5 hr. at room temperature and atmospheric pressure on being shaken with pre-reduced Adams catalyst. No further consumption of hydrogen occurred during the following half-hour. Hydrogenolysis of the benzyl ether linkages and saturation of the aromatic rings requires 8 molar equivalents of hydrogen or 2.0 mmoles.

Anal.[3] Calcd. for $C_{23}H_{30}O_6$ (402.47): C, 68.63; H, 7.51; $(CH_3)_2CO$, 14.4. Found: C, 69.72; H, 7.40; $(CH_3)_2CO$, 14.0.

(1) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath Co., Boston, Mass., 1941, p. 385.

(2) L. F. Wiggins, *J. Chem. Soc.*, 384 (1946). Our sample was prepared from the 1,6-ditosyl-2,5-diacetyl derivative.

(3) Carbon–hydrogen by the Micro-Tech Laboratories, Skokie, Ill. Acetone was determined by the method of Block and Bolling (R. J. Block and D. Bolling, "The Amino Acid Composition of Proteins and Foods," Thomas, Springfield, Ill., 1940, p. 223) after hydrolysis of the samples in the apparatus of Lester and Greenberg [*J. Biol. Chem.*, **154**, 177 (1944)].

DEPARTMENT OF BIOCHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN
LAURENS ANDERSON
ARTHUR J. LUEPTOW
HENRY A. LARDY

RECEIVED APRIL 23, 1951

N-(2-Phenyl-2-ethoxyethyl)-2′-chloroethylamine Hydrochloride

A mixture of 6.0 g. (0.03 mole) of N-(2-phenyl-2-ethoxyethyl)-2-hydroxyethylamine[1] and 4.3 g. (0.036 mole) of purified thionyl chloride in 30 ml. of dry benzene was refluxed for nine hours. The solid, which precipitated during this period of reflux, was recrystallized from isopropyl alcohol, using charcoal to decolorize the solution. Four grams of product (51%), melting at 138–139° (cor.), was obtained.

Anal. Calcd. for $C_{12}H_{18}ClNO \cdot HCl$: N, 5.30. Found: N, 5.28.

(1) I. A. Kaye and I. C. Kogon, THIS JOURNAL, **73**, 4893 (1951).

DEPARTMENT OF CHEMISTRY
BROOKLYN COLLEGE
BROOKLYN 10, NEW YORK
IRVING ALLAN KAYE
IRVING C. KOGON

RECEIVED MAY 12, 1951

Hexamethylenetetramine Salt of α-Bromobutyrolactone

To a solution of 140.1 g. (1.0 mole) of hexamethylenetetramine in 1750 ml. of hot 95% ethanol was added 165 g. (1.0 mole) of α-bromobutyrolactone.[1] After 22 hours at room temperature, the mixture was filtered and the precipitate washed with ethanol followed by ether. The white crystalline water-soluble product weighed 112.1 g. (37%) and melted with decomposition at 155.5–156° (cor.).

Anal. Calcd. for $C_{10}H_{17}BrN_4O_2 \cdot 2H_2O$: C, 35.21; H, 6.20. Found: C, 35.30; H, 6.20.

5-(β-Isothiuroniumethyl)-hydantoin Bromide.—The intermediate, 5-(β-bromoethyl)-hydantoin, was prepared by

(1) J. E. Livak, E. C. Britton, J. C. Vander Weele and M. F. Murray, THIS JOURNAL, **67**, 2218 (1945). The yield of α-amino-γ-butyrolactone hydrobromide prepared by these investigators is incorrectly reported as 59.3%; it should be 50.8%. Following their directions the author obtained a 53.8% yield.

modifying the method of Livak, *et al.*[1] The over-all yield was increased and the method simplified when the α-amino-γ-hydroxybutyric acid needed for the preparation of the 5-(β-bromoethyl)-hydantoin was not isolated.

α-Bromo-γ-butyrolactone (462 g., 2.8 moles) was added, at such a rate that the temperature did not exceed 25°, with stirring to 985 ml. of concentrated ammonia water. After standing overnight at room temperature, a solution of 157 g. of potassium hydroxide in 2575 ml. of water was added. The solution was concentrated to a volume of *ca.* one liter. A solution of 174 g. (2.15 moles) of potassium cyanate in 334 ml. of water was added to the hot solution and the clear reddish-brown solution which resulted was heated at an internal temperature of 65° for two hours. Fourteen hundred ml. of 48% hydrobromic acid was then added to the chilled solution, which was then heated in a steam-bath (internal temperature was 93°) for two hours. After distilling to dryness *in vacuo*, the residue was suspended in two liters of boiling acetone. The mixture was filtered and the insoluble salts were washed well with hot acetone. The solvent was removed from the filtrate by distillation and the residue was heated with 1350 ml. of 48% hydrobromic acid in a steam-bath for two hours. The solution was taken to dryness *in vacuo* and the crude product remaining was dissolved in 400–500 ml. of boiling water. On chilling in an ice-bath, a tan precipitate appeared. This was filtered, washed with ice-water, and recrystallized from one liter of water. The product melted at 139–141° (uncor.) and weighed 142 g. (24.5%). Livak, *et al.*,[1] obtained their 5-(β-bromoethyl)-hydantoin in an 18.6% over-all yield and reported a melting point of 141.5–142°.

A solution of 41.4 g. (0.2 mole) of 5-(β-bromoethyl)-hydantoin and 16.8 g. (0.22 mole) of thiourea in 75 ml. of absolute ethanol was refluxed for 28.5 hours. After chilling in an ice-bath, the precipitate was separated and washed with ethanol followed by ether. The tan solid melted with decomposition at 191–192° (cor.) and weighed 51.5 g. (91%). When the volume of ethanol was decreased to 50 ml., the yield was increased to 95% but the product then melted at 186.5–189.5°.

Anal. Calcd. for $C_6H_{11}BrN_4O_2S$: C, 25.45; H, 3.92. Found: C, 25.79; H, 3.98.

DEPARTMENT OF CHEMISTRY
BROOKLYN COLLEGE
BROOKLYN 10, NEW YORK IRVING ALLAN KAYE

RECEIVED MAY 12, 1951

N-(*p*-Dimethaminobenzyl)-aminoethanol

A warm solution of 74.6 g. (0.5 mole) of *p*-dimethylaminobenzaldehyde and 40 g. (0.66 mole) of ethanolamine in 100 ml. of absolute ethanol was hydrogenated at an initial pressure of 58 lb. in the presence of 250 mg. of platinum oxide. About ten hours was required for the reduction. The catalyst and solvent were removed and the residue vacuum distilled. The product, a pale yellow viscous liquid, weighed 139.2 g. (76%), b.p. 157–158° (1.5 mm.).

Anal. Calcd. for $C_{11}H_{18}N_2O$: N, 14.30. Found: N, 14.28.

DEPARTMENT OF CHEMISTRY
BROOKLYN COLLEGE
BROOKLYN 10, NEW YORK IRVING ALLAN KAYE

RECEIVED MAY 12, 1951

COMMUNICATIONS TO THE EDITOR

ON THE MECHANISM OF THE *IN VIVO* SYNTHESIS OF D-RIBOSE[1]

Sir:

The *in vivo* synthesis of D-ribose in the chick has been studied to determine whether the major pathway is by direct conversion from hexose.[2] Such a conversion would be expected to yield ribose labeled similarly to glycogen after feeding a C^{14}-labeled compound.

In a representative experiment, 7 chicks 1 month old were fasted for 48 hours and fed 6 mM. of sodium acetate containing 72×10^6 counts/minute/mg. of carboxyl carbon and 15 g. of chick mash per 100 g. body weight. After 18 hours, the animals were sacrificed. Glycogen was isolated from a cold trichloroacetic acid extract of the pooled internal organs and muscle and degraded by the method of Wood, *et al.*[3] Ribose was obtained from the purine nucleotide fraction of the trichloroacetic acid insoluble residue. The sodium nucleates were isolated,[4] the pentose and desoxypentose nucleic acids separated[5] and the purine ribonucleotides hydrolyzed with dilute acid. Ribose was purified by two filter paper chromatographic separations using ethyl acetate–acetic acid–water (3:1:3)[6] and *n*-butanol–ethanol–water (4.5:0.5:5) as solvents. A portion of the pentose was fermented with *Lactobacillus pentosus* 124-2 to acetate and lactate followed by further degradation to give the individual carbons as carbon dioxide. The remainder of the ribose was converted to potassium ribonate[7] and the salt oxidized with periodate as a check on the fermentation results. The work of Lampen, *et al.*,[8] has indicated that in this fermentation the α and carboxyl carbons of the acetate arise from pentose carbons 1 and 2, respectively; the carboxyl, α and β carbons of the lactate, from carbons 3, 4 and 5. The data being reported are in agreement with this interpretation.

The values,[9] in counts/minute/mg. carbon, obtained in this experiment for glycogen and ribose by fermentation were

	C_1	C_2	C_3	C_4	C_5	C_6
Glycogen	39	21	2460	2460	21	39
	C_1	C_2	C_3	C_4	C_5	
Ribose	45	52	338	10	0	

(1) Sponsored in part by a grant of the American Cancer Society. The C^{14} used was obtained on allocation from the Atomic Energy Commission.

(2) F. Dickens, *Biochem. J.*, **32**, 1626, 1645 (1938); F. Dickens and G. E. Glock, *Nature*, **166**, 33 (1950); B. L. Horecker and P. Z. Smyrniotis, *Arch. Biochem.*, **29**, 232 (1950); D. B. McNair Scott and S. S. Cohen, *J. Biol. Chem.*, **188**, 509 (1951).

(3) H. G. Wood, N. Lifson and V. Lorber, *ibid.*, **159**, 475 (1945).

(4) J. N. Davidson and C. Waymouth, *Biochem. J.*, **38**, 375 (1944).

(5) G. Schmidt and S. J. Thannhauser, *J. Biol. Chem.*, **161**, 83 (1945).

(6) M. A. Jermyn and F. A. Isherwood, *Biochem. J.*, **44**, 402 (1949).

(7) S. Moore and K. P. Link, *J. Biol. Chem.*, **133**, 293 (1940).

(8) J. O. Lampen, H. Gest and J. C. Sowden, *J. Bact.*, **61**, 97 (1951).

(9) Values have been corrected for addition of carrier during degradation. Radioactivity measurements were made on $BaCO_3$ with an end-window Geiger–Müller counter. Measurements on ribose and ribonate were checked with a gas phase counter at the Brookhaven National Laboratory by Dr. Robert Steele whose assistance is greatly appreciated.