Anal. Calcd. for $C_{14}H_{21}O_7As$: As, 19.92. Found: As, 19.90, 19.98.

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Reaction of Polyethylenepolyamines with *p*-Dichloroarsinobenzoyl Chloride[1]

BY ROBERT L. MCGEACHIN AND OLIVER RAYMOND HUNT, JR.[2]

Doak, Eagle and Steinman[3] and Gough and King[4] have prepared many derivatives and homologs of *p*-arsenosobenzamide by the reaction of *p*-dichloroarsinobenzoyl chloride on various aliphatic amines. However, the reaction of *p*-dichloroarsinobenzoyl chloride with polythylenepolyamines has not previously been reported. We have studied the reaction with diethylenetriamine, aminoethylethanolamine, triethylenetetramine and tetraethylenepentamine. In a preliminary study of the reaction of *p*-dichloroarsinobenzoyl chloride with amino compounds we have also used several amines not previously tried, allylamine, monoisopropanolamine and morpholine.

In the preparation of *p*-benzarsonic acid (from which the *p*-dichlorarsinobenzoyl chloride is made) *via* the Bart reaction on *p*-aminobenzoic acid our yields were comparable with those reported by Lewis and Cheetham[5] and Lewis and Hamilton.[6] However, we have found that this procedure does not give a pure product directly. Only after four or five recrystallizations from alcohol, accompanied by a considerable loss in yield, does the analysis of the product agree with theoretical arsenic percentage. However, the impurities apparently are eliminated in the conversion of the *p*-benzarsonic acid to *p*-dichloroarsinobenzoyl chloride so that the initial crude *p*-benzarsonic acid may be used without further purification.

The reactions of diethylenetriamine and aminoethylethanolamine with *p*-dichloroarsinobenzyl chloride gave satisfactory products when a ten molar excess of the amines were used but triethylenetetramine and tetraethylenepentamine did not. Even when as high as a twenty molar excess of these amines were used, the products obtained contained from 4–7% excess arsenic indicating considerable formation of bis-compounds. Attempts to separate pure products from these mixtures were unsuccessful. Allylamine and monoisopropanolamine gave satisfactory products but with morpholine a pure product could not be isolated because of the extremely high water solubility.

Experimental

Reaction of *p*-Dichloroarsinobenzoyl Chloride with Amines.—These reactions were carried out following the method of Lewis and Hamilton[6] using a five molar excess of allylamine, monoisopropanolamine and morpholine, a ten molar excess with diethylenetriamine and aminoethylethanolamine and a 20 molar excess with tetraethylenepentamine and triethylenetetramine. All products were isolated as the arsenoso compounds by washing with bicarbonate, dissolving in sodium hydroxide solution, reprecipitating by addition of concd. hydrochloric acid and drying at 120°.

TABLE I

SUBSTITUTED *p*-ARSENOSOBENZAMIDES

Amine used	Formula	Analyses,[7] % Calcd.	Found
Allylamine	$C_{10}H_{10}O_2NAs$	29.8	29.3
Monoisopropanolamine	$C_{10}H_{12}O_3NAs$	27.7	27.1
Diethylenetriamine	$C_{11}H_{16}O_2N_3As$	25.3	25.8
Aminoethylethanolamine	$C_{11}H_{15}O_3N_2As$	25.1	25.0

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Wolff–Kishner Reduction of Pyruvic and 3-Formylpropionic Acids[1]

BY E. H. MOSBACH, E. F. PHARES AND S. F. CARSON

The Wolff–Kishner reduction has been applied to a large number of organic compounds,[2] but very few investigations have been reported concerning the reduction of low molecular weight aldehydo- and keto-acids. We have found that pyruvic-2-C^{14} acid and 3-(formyl-C^{14})-propionic acid could be reduced to propionic-2-C^{14} acid and butyric-4-C^{14} acid, respectively, in good yield. These and similar transformations have been used in this Laboratory for the synthesis and degradation of biochemically important compounds.

Table I summarizes specific radioactivity data determined in connection with the synthesis and stepwise degradation[3] of propionic-2-C^{14} acid. This compound was degraded in order to determine whether any rearrangement of the carbon skeleton had occurred during the reduction.

TABLE I

SYNTHESIS AND DEGRADATION OF PROPIONIC-2-C^{14} ACID

Compound or carbons	Specific radioactivity,[a] counts/min./mg. $BaCO_3$ Calcd.	Found
Pyruvic-2-C^{14} acid	..	126
Propionic-2-C^{14} acid	15.8[b]	16.2
Carbon 1	0.0	0.1
Carbon 2	47.4	46.1
Carbon 3	0.0	0.1

[a] $BaCO_3$ from wet combustion, G–M counting at infinite thickness, estimated over-all precision of radioassay ±5%. [b] Eight-fold dilution with non-radioactive carrier.

Table II shows similar data for the preparation of butyric-4-C^{14} acid from glutamic-1,2-C_2^{14} acid. This reaction was carried out by converting glutamic acid quantitatively to 3-formylpropionic acid with chloramine T, followed by a Wolff–Kishner reduction of the aldehydo-acid. As before, a step-

(1) This work was aided by a grant to the University of Louisville from the Kentucky State Medical Research Commission.

(2) Research Scholar 1949–1950. Present address: Edward W. Sparrow Hospital, Lansing, Michigan.

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wise degradation[4] of the fatty acid was carried out to determine the position of the radioactive label.

TABLE II

SYNTHESIS AND DEGRADATION OF BUTYRIC-4-C^{14} ACID

Compound or carbons	Specific radioactivity,[a] counts/min./mg. $BaCO_3$ Calcd.	Found
Glutamic-1,2-C_2^{14} acid	...	7.50
3-(Formyl-C^{14})-propionic acid	4.69[b]	...
Butyric-4-C^{14} acid	4.69	4.72
Carbon 1	0.0	0.05
Carbon 2	0.0	0.04
Carbon 3	0.0	0.24
Carbon 4	18.8	18.1

[a] See footnote for Table I. [b] Calculated from specific activity of glutamic-1,2-C_2^{14} acid.

The data of Tables I and II indicate that under the conditions of the Huang-Minlon modification[2] of the Wolff–Kishner reduction there occurred no detectable rearrangement of the carbon skeleton of pyruvic and 3-formylpropionic acids. It is believed that the appreciable radioactivity found for carbon 3 of butyric-4-C^{14} acid was probably not caused by the reduction or the degradation procedure, but may have been introduced during the synthesis of the labeled starting material.[5]

Experimental

Propionic-2-C^{14} Acid.—Carbonyl-labeled pyruvic acid (1.0 mmole) prepared by the method of Anker[6] was purified by partition chromatography. The aqueous solution of the sodium salt (0.85 mmole) obtained from the partition column was concentrated to a volume of 5 ml. in a 200-ml. flask. Redistilled diethylene glycol (25 ml.), 5 ml. of an 85% hydrazine solution and 1 g. of potassium hydroxide were added and the solution was refluxed for one hour. Water was then distilled off until the temperature reached 190°, and heating under reflux was continued for one hour. The reaction mixture was cooled, acidified with sulfuric acid and steam distilled. The steam distillate was concentrated and propionic acid was obtained in aqueous solution, as the sodium salt, by partition chromatography.[7] The chromatographic step was required in order to separate propionic acid from traces of acetic acid formed by thermal decomposition of the solvent. Propionic acid was identified by its position on the chromatogram, Duclaux distillation and preparation of the *p*-bromophenacyl ester, m.p. 59–60°; yield 73% of the theoretical based on sodium pyruvate.

Butyric-4-C^{14} Acid.—Because of its instability, 3-(formyl-C^{14})-propionic acid was prepared as needed by treating glutamic-1,2-C_2^{14} acid with an equimolecular amount of chloramine T at 50°.[8] It was found that this reagent converted glutamic acid quantitatively to 3-formylpropionic acid. The latter was not isolated from solution but was identified and weighed as the *p*-nitrophenylhydrazone, m.p. 178–180°, and the 2,4-dinitrophenylhydrazone, m.p. 198–200°. The aqueous solution of 3-(formyl-C^{14})-propionic acid was taken directly for the Wolff–Kishner reduction as described for propionic-2-C^{14} acid. Butyric-4-C^{14} acid was isolated by partition chromatography[7] and identified by its position on the chromatogram, Duclaux distillation and preparation of the *p*-bromophenacyl ester, m.p. 63–64.5°; yield 55% of theory based on glutamic acid.

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BIOLOGY DIVISION
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENN. RECEIVED MAY 17, 1951

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Preparation of Sodium Ferrate(VI)

BY LOUIS T. OCKERMAN AND JAMES M. SCHREYER

Numerous wet methods for the preparation of solutions of sodium ferrate, Na_2FeO_4, have been reported. Foster,[1] Thiesse,[2] Rosell,[3] and Grube and Gmelin[4] prepared such solutions by different oxidation methods, but were unable to isolate any solid Na_2FeO_4.

Wallace and Fleck[5] prepared crystalline Na_2FeO_4 by fusion of Na_2O_2 in an iron crucible. The crystals were described as probably being pure Na_2FeO_4, although no analysis was reported.

In view of the failure of previous investigators to prepare crystalline Na_2FeO_4 by wet methods, the authors made a further study of the problem.

Experimental

Chlorine gas was passed into a solution containing 30 g. of solid NaOH per 75 ml. of water until the increase in weight amounted to 20 g. The temperature was maintained below 20° by means of an ice-bath. After the dissolution of 70 g. of solid NaOH, the solution was filtered. The beaker containing the solution was replaced in the ice-bath and 20 g. of ferric nitrate was added. The solution was cooled to 10–15° and saturated by adding solid NaOH. The solution was filtered through a fritted glass filter and the black mass was air dried by continued suction. A small volume of benzene was drawn through the mass on the filter, followed by 3 portions of 95% ethanol. Each portion was left in contact with the black mass for only a few minutes. The product was finally dried with a few milliliters of ethyl ether. A calcium chloride drying tube was attached to the mouth of the filter during the final drying operation.

The solid product obtained by the above procedure gave a purple color characteristic of the ferrate ion when added to water.

Although the sample appeared to be highly contaminated with hydrous ferric oxide, analysis by the chromite method[6] showed 41.38% Na_2FeO_4.

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UNIVERSITY OF KENTUCKY
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Steroids. XXI.[1] Δ^7-Androstene-3β,17β-diol

BY F. NEUMANN, G. ROSENKRANZ, J. ROMO AND CARL DJERASSI

Steroids with an isolated double bond in the 7,8-position are of considerable importance[2,3] for biological experiments and synthetic purposes. Since no such representative is known in the androstane series, we have investigated two obvious synthetic routes as outlined below.

The first approach consisted of catalytic hydrogenation of $\Delta^{5,7}$-androstadiene-3β,17β-diol (IIa) to yield Δ^7-androstene-3β,17β-diol (IVa). The former substance has been prepared before by an

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