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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[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.

[3] G. O. Doak, H. Eagle and H. G. Steinman, THIS JOURNAL, **62**, 3012 (1940).

[4] G. A. C. Gough and H. King, *J. Chem. Soc.*, 669 (1930).

[5] W. L. Lewis and H. C. Cheetham, THIS JOURNAL, **43**, 2117 (1921).

[6] W. L. Lewis and C. S. Hamilton, *ibid.*, **45**, 757 (1923).

[7] A modification of the method of F. E. Cislak and C. S. Hamilton, *ibid.*, **52**, 638 (1930), was used in the arsenic analyses.

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-

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[1] Work performed at the Oak Ridge National Laboratory under Contract No. W-7405-Eng-26 for the Atomic Energy Commission.

[2] R. Adams, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., Chap. 8, 1946.

[3] E. F. Phares, *Arch. Biochem. Biophys.*, **33**, 173 (1951).