Experimental

4,5-Dibromoguaiacol can be purified by boiling with 20% NaCl solution. The melting point of the substance prepared by this steam distillation is 94–95°. Methylation yields 4,5-dibromoveratrol, m.p. 92–93°. Dibromoguaiacol acetate melts at 101–102° in accordance with the value of Raiford and Silker[2]; m.p. of the benzoate 112–113° (Raiford and Silker[2] 110–111°).

Reduction of Tribromoguaiacol (II) with Zinc Dust and Acetic Acid.—Fourteen grams of tribromoguaiacol, 9 g. of zinc dust, 40 ml. of glacial acetic acid and 10 ml. of water were boiled under reflux for 4 minutes. The mixture was cooled, filtered and pieces of ice added. The oily precipitation solidified. The substance was filtered by suction, dried in vacuum (6 g.), triturated with petrol ether (b.p. 60–110°), filtered by suction and recrystallized from petrol ether; m.p. 94–95°.

Anal. Calcd. for $C_7H_6O_2Br_2$: Br, 56.73. Found: Br, 57.06, 56.87.

The melting points of its acetate, benzoate and methyl ether were in agreement with the values given above.

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Some 5-Alkyl-1-acetyl-2-thiohydantoins[1]

BY J. F. R. KUCK, J. J. HERDA, W. E. KOVAC AND J. V. KARABINOS

In the course of some work on the chromatography of amino acid derivatives in this Laboratory, we found it necessary to prepare 5-alkyl-1-acetyl-2-thiohydantoins from a number of α-amino acids.

One-hundredth of a mole of amino acid was heated with 0.9 g. of ammonium thiocyanate in 10 ml. of acetic anhydride containing 1.3 ml. of acetic acid for 30 minutes at 100°. After the reaction mixture was poured into 50 ml. of water an oil separated from which the acetylthiohydantoin subsequently crystallized. Further purification was accomplished by recrystallization of the crude product from ethanol. For purposes of identification the melting points and analyses of the derivatives prepared in this study are listed in Table I along with the others previously reported. The amino acids which failed to give a precipitate upon addition to water included DL-serine, DL-threonine, L-tyrosine, L-proline and L-hydroxyproline as well as the monohydrochlorides of L-histidine, L-arginine, L-lysine and DL-ornithine. This may indicate the use of this reaction for the group separation of mixtures of the amino acids.

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TABLE I

5-ALKYL-1-ACETYL-2-THIOHYDANTOINS R—CH—CO—NH—CS—N—$COCH_3$

R–	Amino acid	M.p., °C.	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Isopropyl-	DL-Valine	115	47.98	47.92	6.04	6.27
n-Butyl-	DL-Norleucine	136	50.44	50.63	6.58	6.89
s-Butyl-	DL-Isoleucine	163	50.44	50.62	6.58	6.61
Methylthioethyl-	DL-Methionine	104	41.35	41.50	5.21	5.22
β-Amidoethyl-	L-Glutamine[a]	219	41.91	42.24	4.84	4.90
Indole-β-methyl-	DL-Tryptophan	170	58.52	58.50	4.56	4.27
p-Hydroxybenzyl-	L-Tyrosine[a]	248[b]	54.53	54.73	4.58	4.26
Hydrogen	Glycine	179[c]	37.96	38.21	3.82	3.63
Bis-thiomethyl-	L-Cystine[a]	208[d]				
s-Acetylthiomethyl-	L-Cysteine[a]	142[e]				
i-Butyl-	DL-Leucine[a]	129[f]				
Benzyl-	DL-Phenylalanine[a]	170[g]				
Amidomethyl-	DL-Asparagine[a]	224[g]				
Methyl-	DL-Alanine[a]	166[g]				

[a] Actually the optical identity of these acetylthiohydantoins is uncertain since acetic anhydride frequently acts as a racemizing agent. Furthermore the optical configuration of some of the amino acids was not given in the original reference and can only be surmised. [b] The oil which was precipitated by adding water was dissolved in 10 ml. of 5% sodium hydroxide and the yellow solution was filtered. The chilled filtrate was added slowly with stirring to a slight excess of 10% hydrochloric acid. The amorphous solid which separated was recrystallized from ethanol. The preparation reported was obtained only once; this procedure usually gave the unacetylated compound, 5-*p*-hydroxybenzyl-2-thiohydantoin of m.p. 211°. *Cf.* M. Jackman, *et al.*, THIS JOURNAL, **70**, 2884 (1948). [c] T. B. Johnson and B. H. Nicolet, *ibid.*, **33**, 1973 (1911). [d] B. H. Nicolet, *J. Biol. Chem.*, **88**, 395 (1930). [e] *Ibid.* [f] P. Schlack and W. Kumpf, *Z. physiol. Chem.*, **154**, 125 (1926). [g] Ref. 2.

Although several of these derivatives were known, we wish to report the preparation of additional ones and describe a method for obtaining crystalline derivatives of most of the naturally occurring monoamino-monocarboxylic acids, essentially according to the directions of Johnson and Nicolet.[2]

(1) Research supported by the Office of Naval Research under contract N7ONR-449.

(2) T. B. Johnson and B. H. Nicolet, *Am. Chem. J.*, **49**, 197 (1913).

The Action of Sodium on Di-*s*-butylmercury

BY JOHN F. LANE AND STEPHEN E. ULRICH

Previous studies in these laboratories[1,2] have shown that the major path of reaction in syntheses of the Wurtz type with *s*-alkyl halides proceeds through (ionic) interaction of an *s*-alkyl sodium with the halide. These studies have not, however, ruled out the possibility that a portion, at least, of the Wurtz product might have resulted from the dimerization of *s*-alkyl radicals formed by thermal dissociation of the *s*-alkyl sodium present, an energetically plausible process.[3] To throw further light upon this matter a study was undertaken on the interaction of sodium with di-*s*-butylmercury, in the hope of producing *s*-butylsodium through displacement of mercury. The interaction of sodium with mercury *n*-alkyls is

(1) S. E. Ulrich, F. H. Gentes, J. F. Lane and E. S. Wallis, THIS JOURNAL, **72**, 5127 (1950).

(2) J. F. Lane and S. E. Ulrich, *ibid.*, **72**, 5132 (1950).

(3) *Cf.* N. G. Brink, J. F. Lane and E. S. Wallis, *ibid.*, **65**, 943 (1943).